

518 Rec'd PCT/PTO 31 JUL 2001

Form PTO-1390 U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE (REV 10-95)		ATTORNEY'S DOCKET NUMBER 1214-011212
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		09/890438
INTERNATIONAL APPLICATION NO. PCT/JP00/00518	INTERNATIONAL FILING DATE 31.01.00 (31 January 2000)	PRIORITY DATES CLAIMED 01.02.99 (01 February 1999)
TITLE OF INVENTION NOVEL CRYSTALLINE ION-ASSOCIATION SUBSTANCE, PROCESS FOR PRODUCING THE SAME, AND POLYMERIZATION INITIATOR		
APPLICANT(S) FOR DO/EO/US Shin HIWASA		
<p>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). <input checked="" type="checkbox"/> has been transmitted by the International Bureau. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> have been transmitted by the International Bureau. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input checked="" type="checkbox"/> have not been made and will not be made. <input checked="" type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). <p>Items 11. to 16. below concern document(s) or information included:</p> <ol style="list-style-type: none"> <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input checked="" type="checkbox"/> Other items or information: <ol style="list-style-type: none"> WO 00/46171-Front Page with Abstract and Search Report (2 pp.) 		

JC17 Rec'd PCT/PTO 31 JUL 2001

U.S. APPLICATION NO.		09/890438		INTERNATIONAL APPLICATION NO. PCT/JP00/00518		ATTORNEY'S DOCKET NUMBER 1214-011212	
17. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO \$860.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) \$690.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))... \$710.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO..... \$1000.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)..... \$100.00						CALCULATIONS PTO USE ONLY	
ENTER APPROPRIATE BASIC FEE AMOUNT =						\$ 860.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).						\$ 0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE				
Total claims	8 - 20	0	X \$18.00	\$ 0.00			
Independent claims	1 - 3 =	0	X \$80.00	\$ 0.00			
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$ 0.00			
TOTAL OF ABOVE CALCULATIONS =				\$ 860.00			
Reduction of 1/2 for filing by small entity, if applicable.				\$ 430.00			
SUBTOTAL =				\$ 430.00			
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$ 0.00			
TOTAL NATIONAL FEE =				\$ 430.00			
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property				\$ 40.00			
TOTAL FEES ENCLOSED =				\$ 470.00			
				Amount to be: Refunded	\$		
				Charged	\$		
a. <input checked="" type="checkbox"/> A check in the amount of \$ 470.00 to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Assistant Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>23-0650</u> . A duplicate copy of this sheet is enclosed.							
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.							
SEND ALL CORRESPONDENCE TO: Barbara E. Johnson 700 Koppers Building 436 Seventh Avenue Pittsburgh, Pennsylvania 15219-1818 Telephone: (412) 471-8815 Facsimile: (412) 471-4094				 SIGNATURE Barbara E. Johnson NAME 31,198 REGISTRATION NUMBER			

518 Rec'd PCT/PTO 31 JUL 2001

09/890438
PATENT APPLICATION/PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:

ATTORNEY'S DOCKET NUMBER

Shin HIWASA

1214-011212

PCT/JP00/00518

ENTITLED

NOVEL CRYSTALLINE ION-ASSOCIATION SUBSTANCE, PROCESS
FOR PRODUCING THE SAME, AND POLYMERIZATION INITIATOR

To BOX PCT

Attention: DO/EO/US

Assistant Commissioner for Patents
Washington, D.C. 20231

EXPRESS MAIL CERTIFICATE

"Express Mail" Label Number EL7635793337US

Date of Deposit July 31, 2001

I hereby certify that the following attached paper or fee

Transmittal Letter To The United States
Designated/Elected Office (DO/EO/US) Concerning A
Filing Under 35 U.S.C. 371 (original and two (2) copies)
And Check In The Amount Of \$470 For Filing Fee and Assignment Fee;
WO 00/44915 Front Page With Abstract (1 p.) And Search Report (1 p.);
Preliminary Amendment;
Specification and Claims (47 pp.);
Translation Of Amendments To The Claims Under Article 19 (4 pp.);
Declaration And Power Of Attorney (2 pp.);
Recordation Form Cover Sheet (1 p.) And Assignment (2 pp.);
Verified Statement Claiming Small Entity Status (2 pp.)

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee"
service under 37 C.F.R. §1.10 on the date indicated above and is addressed to the Assistant
Commissioner for Patents, Washington, D.C. 20231.

K.T. Berthold

(Typed name of person mailing paper or fee)

K.T. Berthold
(Signature of person mailing paper or fee)

Applicant or Patentee: Shin HIWASA Attorney's
Serial or Patent No.: _____ Docket No.: 1214-011212
Filed or Issued: _____

For: Novel Crystalline Ion-Association Substance, Process for
Producing The Same, and Polymerization Initiator
VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(f) & 1.27(c))--SMALL BUSINESS CONCERN

I hereby declare that I am

_____ the owner of the small business concern identified below:
☒ an official of the small business concern empowered to act on behalf
of the concern identified below:
NAME OF SMALL BUSINESS CONCERN AUTEX, INC.
ADDRESS OF SMALL BUSINESS CONCERN Shinjukutakasago Bldg., 16-5, Tomihisacho,
Shinjuku-ku, Tokyo 162-0067, Japan

I hereby declare that the above identified small business concern qualifies as a small business concern as defined in 13 CFR 121.12, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees to the United States Patent and Trademark Office, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled Novel Crystalline Ion-Association Substance, Process for Producing the Same, and Polymerization Initiator by inventor(s) Shin HIWASA

described in

☒ the specification filed herewith.
_____ application serial no. _____, filed _____.
_____ patent no. _____, issued _____.

If the rights held by the above identified small business concern are not exclusive, each individual, concern or organization having rights in the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who would not qualify as an independent inventor under 37 CFR 1.9(c) if that person made the invention, or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d), or a nonprofit organization under 37 CFR 1.9(e). *NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

NAME _____
ADDRESS _____
_____ INDIVIDUAL _____ SMALL BUSINESS CONCERN _____ NONPROFIT ORGANIZATION

NAME _____
ADDRESS _____
_____ INDIVIDUAL _____ SMALL BUSINESS CONCERN _____ NONPROFIT ORGANIZATION

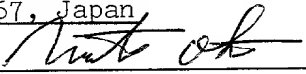
I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING Morito OTA

TITLE OF PERSON IF OTHER THAN OWNER President

ADDRESS OF PERSON SIGNING Shinjukutakasago Bldg., 16-5, Tomihisacho, Shinjuku-ku,
Tokyo 162-0067, Japan

SIGNATURE  DATE July 11, 2001

JC17 Rec'd PCT/PTO 31 JUL 2001

09/890438

PATENT APPLICATION/PCT
Atty. Docket No. 1214-011212

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of :
Shin HIWASA : NOVEL CRYSTALLINE
International Application : ION-ASSOCIATION SUBSTANCE,
No. PCT/JP00/00518 : PROCESS FOR PRODUCING THE
International Filing Date : SAME, AND POLYMERIZATION
31 January 2000 : INITIATOR
Priority Date Claimed :
01 February 1999 :
Serial No. Not Yet Assigned :
Filed Concurrently Herewith :

Pittsburgh Pennsylvania
July 31, 2001

PRELIMINARY AMENDMENT

BOX PCT
Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to initial examination, please amend the above-identified patent application as follows:

IN THE SPECIFICATION:

Please insert section headings and amend specification paragraphs as follows. (Pursuant to 37 CFR 1.121, marked-up versions of the amended specification paragraphs are attached.)

On page 1, after the title, please insert the following section heading.

BACKGROUND OF THE INVENTION

On page 1, please amend the section heading "Technical Field" to read as follows:

1. Field of the Invention

On page 1, please amend the section heading "Background of the Invention" to read as follows:

2. Description of the Related Art

On page 1, please delete the third complete paragraph and insert the following replacement paragraph:

High molecular weight products produced by hardening (or polymerizing) the above-mentioned compounds have various uses, especially epoxy resin and silicone resin which have been widely used as adhesives, sealing, and paints in various fields such as automobile industry, housing/building material industry, civil engineering and construction industries, aircraft industry, and electric and electronic industries.

On page 1, please delete the fifth complete paragraph and insert the following replacement paragraph:

It has been well known that the polymerization is generally carried out at room temperature or under heating conditions. Recently, searches for a photopolymerization catalyst or initiator have been conducted, because it may be preferable to carry out the polymerization under irradiation conditions depending upon use. However, no remarkable result has been obtained.

On page 2, please delete the fourth complete paragraph and insert the following replacement paragraph:

As another example, the photopolymerization initiator disclosed in Japanese Patent Publication No. 62692/94 of the same applicant as this application can be cited. This photopolymerization initiator comprises a composite obtainable from a reaction between (a) charge transfer complex consisting of biscyclopentadienyl iron derivative and quinoid and (b) at least one salt selected from a group consisting of tetrafluoroborates, hexafluorophosphates and hexafluoroantimonates.

On page 2, please delete the fifth complete paragraph and insert the following replacement paragraph:

On the contrary, regarding the photopolymerization of organosiloxane, it is very hard to find an example. An example can be found only in Kevin D. Belfield et al., "Photoinitiated cationic ring-opening polymerization of a cyclosiloxane", Polymer Bulletin 38, pp. 165-168 (1997). Belfield et al. disclosed that when hexamethylene cyclotrisiloxane is exposed with U.V. light in the presence of sulfonium or iodonium salt or iminosulfonate derivative, it is subjected to a photo-initiating cationic ring-opening polymerization in solution or in the absence of solvent.

Please delete the paragraph bridging pages 2 and 3 and insert the following replacement paragraph:

Regarding the thermal hardening (polymerization) reaction which is carried out at room temperature or under heating conditions, as example of catalyst for polymerization of epoxy compound, tertiary amine (such as benzylmethyl amine, 2,4,6-trisdimethylamine methylphenol, etc.), imidazole (such as 2-methylimidazole, 2-ethyl-4-methylimidazole, 2-heptadecylimidazole etc.), Lewis acid (such as BF_3 monoethylamine, BF_3 piperazine, etc.) have been known.

On page 3, please delete the first complete paragraph and insert the following replacement paragraph:

The thermal hardening reaction of organosiloxane compound is classified into addition type and condensation type: in a reaction of the former type, peroxide or platinum compound is used as catalyst and in a reaction of the latter type, metal salt of carboxylic acid is used.

On page 3, please delete the second complete paragraph and insert the following replacement paragraph:

As mentioned above, epoxy resins and silicone resins have been widely used. However, on producing the epoxy resins or silicone resins by hardening (or polymerizing) each monomer, the catalyst or initiator used in the thermal polymerization or photopolymerization of epoxy compound is completely different from that used in the thermal polymerization or photopolymerization of organosiloxane compound, and additionally, an initiator for photopolymerization of organosiloxane compound is almost unknown.

On page 3, please amend the section heading "Disclosure of the Invention to read as follows:

Summary of the Invention

On page 4, please amend the section heading "Best Mode for Carrying out the Invention" to read as follows:

Description of the Preferred Embodiments

On page 4, please delete the third complete paragraph which begins with "The crystalline" and insert the following replacement paragraph:

The crystalline ion-association substance of the present invention comprises, as is seen from the general formula (I), a metallocene derivative cation and a tetradentate borate complex anion wherein the four ligands are the same to each other.

Please delete the paragraph bridging pages 4 and 5 and insert the following replacement paragraph:

In the general formula (I), the electron donative or electron attractive substituent is alkyl group, cycloalkyl group, aryl group, alkoxy group, silyl group, dialkyl group, acyl group, cycloalkenyl group, amino group, carboxyl group, organoboranyl group, phosphino group, aldehyde group, hydroxyl group and the like. More particularly, the alkyl group is selected from among lower alkyl groups such as methyl group, ethyl group, propyl group and butyl group, or pentyl group or amyl group; and the cycloalkyl group is selected from among cyclobutyl group, cyclopentyl group, cycloheptyl group, and cyclohexyl group. The aryl group is selected from among phenyl group, naphtyl group, etc.

On page 6, please delete the paragraph which begins with "On the other hand,".

Before the paragraph bridging pages 6 and 7, please insert the following paragraph:

On the other hand, the counter anion of the crystalline ion-association substance of the present invention is tetradentate borate complex anion $[B(R^2)_4]^-$. In the formula, R^2 is a ligand coordinated to boron atom (B) of the center nucleus and is selected from among aryl group, halogenated aryl group, halogen haloformaryl group, cycloalkynyl group, halogenated cycloalkyl group, halogenated cycloalkynyl group, cycloalkyloxy group, cycloalkenyloxy group, alkadienyl group, alkatrienyl group, alkynyl group, halogenated

alkenyl group, halogenated alkadienyl group, halogenated alkatrienyl group, halogenated alkynyl group, heterocyclic group, etc., but the four ligands (R^2) are the same to each other. Also, the two adjacent ligands may chemically bond to each other to form two rings bonding the ligands within one borate complex anion.

On page 8, please delete the first complete paragraph and insert the following replacement paragraph:

The crystalline ion-association substance of the present invention contains a bulky ligand in the cyclopentadienyl moiety of the metallocene derivative cation. Therefore, a transition metal of the center nucleus having a high oxidation state may maintain thermal stability, and the crystallinity between the metallocene derivative cation and the anion complex to be associated is synergistically increased.

On page 11, please delete the first complete paragraph and insert the following replacement paragraph:

The crystalline ion-association substance of the present invention may have such a structure that one of four identical ligands of the borate complex anion is closed to the transition metal center of the metallocene derivative cation and is sandwiched between the two cyclopentadiene ligands of the metallocene derivative cation; the metallocene derivative cation per se having such a structure that the two cyclopentadiene ligands with various structure are positioned in the form of a dihedral structure with respect to the transition metal center.

Please delete the paragraphs bridging pages 11 and 12 and insert the following replacement paragraph:

In photopolymerization of a cationically polymerizable organic substance, the polymerization initiator of the present invention is used in the amount of from 0.1 to 10 weight parts, preferably 0.5 to 4 weight parts with respect to 100 weight parts of the

On page 18, please delete the second paragraph and insert the following replacement paragraph:

In preparation of the crystalline ion-association substance of the present invention, commercially available products (for example, products sold by Tokyo Chemicals Co. or Aldrich Co.) can be used as metallocene derivative. Other metallocene derivatives can be prepared by the well-known methods for preparation disclosed in the following references:

On page 22, please delete the first complete paragraph and insert the following replacement paragraph:

By using a similar apparatus and procedure to those used in Example 4, 0.46g of (dihydroxyboryl) ferrocenium/tetrakis(3,5-difluorophenyl) borate was obtained (yield 51%), starting from 0.3g of commercially available ferroceneboronic acid (CAS 12152-94-2), 0.021g of iron(III) chloride, 30ml of acetonitrile, 10ml of pure water and 0.635g of tetrakis (3,5-difluorophenyl) borate sodium salt.

On page 23, please delete the second complete paragraph beginning with "By using".

On page 23, after the section heading under "Example 8" please insert the following new paragraph:

By using similar apparatus and procedure to those used in the Example 1, 1.36g of dimethyl ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate was obtained (yield 54.1%), starting from 0.5g of dimethyl ferrocene, 10g of conc. Sulfuric acid, and ethanol solution (7ml) containing 2.15g of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate sodium salt.

Please delete the paragraph bridging pages 26 and 27 and insert the following replacement paragraph:

On the other hand, in case of using an organosiloxane compound having volatility and subliming property, a test sample was prepared as follows:

In a similar bottle to that described above, 10 weight parts of dichloromethane is added with respect to 100 weight parts of the organosiloxane compound, and then the predetermined amount of polymerization initiator is added thereto. The resulting liquid mixture is stirred to disperse the initiator. Thereafter, the liquid mixture enclosed in the bottle is irradiated repeatedly with U.V. light ($6000\text{mJ}/\text{cm}^2$) four times from outside of the bottle. The obtained test sample (rubber-like hardened product produced in the bottle) is taken out and transferred to a glass cylinder for Soxhlet extraction test (glass filter with filter plate No. GP-100) to measure gel fraction.

On page 32, please delete the second complete paragraph and insert the following replacement paragraph:

To 100 weight parts of decamethylcyclopentasiloxane (D5) or dodecamethylcyclohexasiloxane (D6), 2 weight parts of each polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 8 or 10, 4 weight parts of benzophenone (sensitizer) and 30 weight parts of dichloromethane were added. The obtained mixture was stirred and mixed to prepare a solution in which the organosiloxane compound, the sensitizer and the polymerization initiator were homogeneously dissolved in the solvent. The obtained solution was fed to the center recess of the hole slide glass of one hole type without overflowing the solution from the recess. The hole slide glass was put into a hot air circulating oven and maintained at 60°C for 10 min. The test film was cooled to room temperature and irradiated with U.V. light ($600\text{ mJ}/\text{cm}^2$). The gel fraction of the hardened films was reported in the following Table 4.

On page 33, please delete the second complete paragraph and insert the following replacement paragraph:

To 100 weight parts of 1,3-bis(glycidoxypropyl) tetramethyldisiloxane (silicone-modified epoxy monomer) (Gelest Inc.; SIH1115.0; CAS 126-80-7), 1 weight part of each polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 2, 3, 8, 9, 10, 11, 12 or 13, 2 weight parts of benzophenone (sensitizer) and 50 weight parts of dichloromethane were added. The obtained mixture was stirred and mixed to prepare a solution in which the silicone-modified epoxy compound, the sensitizer and the polymerization initiator were homogeneously dissolved in the solvent. The obtained solution was fed to the center recess of the hole slide glass of one hole type without overflowing the solution from the recess. The hole slide glass was put into a hot air circulating oven and maintained at 60°C for 10 min. and then at 80°C for 3 min. Each test film was irradiated with U.V. light (8000mJ/cm²).

On page 40, please delete the first complete paragraph and insert the following replacement paragraph:

These examples show the fact that the polymerization initiator which comprises the crystalline ion-association substance prepared in the above-mentioned Example 3, 9, 11 or 12 has an ability to produce a thermal polymerization of a mixture consisting of cyclic siloxane and epoxy compound.

On page 42, please delete the first complete paragraph beginning with "The polymerization" and insert the following replacement paragraph:

The polymerization initiator of the present invention has the unique property that it can initiate both photopolymerization and thermal polymerization when used in polymerizing cationically polymerizable organic substance, though the polymerization initiator comprises an identical crystalline ion-association substance.

On page 42, please delete the second complete paragraph beginning with "In particular" and insert the following replacement paragraph:

In particular, since the photopolymerization initiator for organosiloxane has been little developed, the polymerization initiator of the present invention is valuable.

Please delete the paragraph bridging pages 42 and 43 and insert the following replacement paragraph:

For the above-mentioned unique property of the polymerization initiator of the present invention, it is possible to obtain a merit in practical use; that is, after the U.V. light irradiation, it is possible to carry out the hardening in a shade zone which is not exposed to U.V. light or a deep zone to which U.V. light does not reach by means of heating (photopolymerization plus thermal polymerization). This merit is very important, because, in accordance with conventional method, when the hardening is carried out by using both means of photopolymerization and thermal polymerization in accordance with conventional method, it is necessary to modify a monomer itself; for example, to prepare a modified organosiloxane having epoxy group.

On page 43, please delete the last complete paragraph and insert the following replacement paragraph:

Therefor, it is possible to extend the field and method for use of cationically polymerizable organic substances by using the polymerization initiator of the present invention.

IN THE CLAIMS:

Please cancel original claims 1-10 and cancel amended claims 7-15 and rewrite them as new claims 16-23 as follows:

16. A polymerization initiator for a cationically polymerizable organic substance, wherein said polymerization initiator comprises a crystalline ion-association substance having the general formula (I):



wherein M is a transition metal of center nucleus; C₅ is a cyclopentadienyl group; R¹ is an electron donative or electron attractive substituent bonded to a carbon atom of cyclopentadienyl group, or an organic group bridging two neighboring carbon atoms; n is a number within range of 0 to 3; m is either 1 or 2; 1 is either 1 or 2; R² is a ligand coordinated to boron atom (B), and the four R²(s) are the same to each other.

17. The polymerization initiator claimed in claim 16, wherein said cationically polymerizable organic substance is a compound or mixture of at least two compounds selected from the group consisting of methylol compounds, ethylenic compounds, polyacetal compounds, organosiloxane compounds, polyamide compounds and heterocyclic compounds.

18. The polymerization initiator claimed in claim 17, wherein said cationically polymerizable organic substance is selected from the group consisting of organosiloxane compounds, epoxy compounds and mixtures thereof.

19. The polymerization initiator claimed in claim 16, wherein said transition metal of center nucleus (M) of said general formula (I) is selected from the group consisting of Ti, Zr, Fe, Ru, Os, Hf, V, Cr, Mo and W.

20. The polymerization initiator claimed in claim 16, wherein said electron donative or electron attractive substituent of said general formula (I) is, identical to or different from each other, selected from the group consisting of alkyl group, cycloalkyl group, alkoxy group, aryl group, dialkyl group, silyl group, acyl group, cycloalkenyl group, amino group, carboxyl group, organoboranyl group, phosphino group, aldehyde group, hydroxyl group and vinyl group; and wherein said organic group bridging two neighboring carbon atoms is an alkylene group.

21. The polymerization initiator claimed in claim 16, wherein the crystalline ion-association substance having the general formula (I) comprises a metallocene derivative cation having mono-nucleus structure or di-nucleus structure selected from the group consisting of acetyl ferrocenium, tert.-amyl ferrocenium, benzoyl ferrocenium, n-butyl ferrocenium, cyclohexenyl ferrocenium, cyclopentenyl ferrocenium, 1,1'-diacetyl ferrocenium, 1,1'-di-n-butyl ferrocenium, N,N-dimethylaminomethyl ferrocenium, 1,1'-dimethyl ferrocenium, ethyl ferrocenium, (dihydroxyboranyl) ferrocenium, 1-hydroxyethyl ferrocenium, hydroxymethyl ferrocenium, vinyl ferrocenium, 1,1-bis(diphenylphosphino) ferrocenium, ferrocenium, t-butyl ferrocenium, dibutyl ferrocenium, bis(cyclopentadienyl) chromium cation, bis(cyclopentadienyl) molybdenum chloride cation, bis(cyclopentadienyl) osmium cation, bis(t-butylcyclopentadienyl) titanium chloride cation, bis(cyclopentadienyl) dicarbonyl titanium cation, bis(cyclopentadienyl) titanium chloride cation, bis(cyclopentadienyl) tungsten chloride cation, bis(i-propylcyclopentadienyl) tungsten

chloride cation, vanadocenium, bis(n-butylcyclopentadienyl) zirconium chloride cation, bis(t-butylcyclopentadienyl) zirconium chloride cation, bis(cyclopentadienyl) zirconium chloride cation, bis(ethylcyclopentadienyl) zirconium chloride cation, bis(methylcyclopentadienyl) zirconium chloride cation, bis(indenyl) dimethyl zirconium cation, bis(t-butylcyclopentadienyl) hafnium chloride cation, bis(ethylcyclopentadienyl) hafnium chloride cation, bis(iso-propylcyclopentadienyl) hafnium chloride cation and diferrocenium derivative cation.

22. The polymerization initiator claimed in claim 16, wherein said ligand (R^2) of the said formula (I) is selected from the group consisting of aryl group, halogenated aryl group, halogen haloform aryl group, cycloalkynyl group, halogenated cycloalkyl group, halogenated cycloalkynyl group, cycloalkoxy group, cycloalkenyloxy group, alkadienyl group, alkatrienyl group, alkynyl group, halogenated alkenyl group, halogenated alkadienyl group, halogenated alkatrienyl group, halogenated alkynyl group and heterocyclic group.

23. The polymerization initiator claimed in claim 16, wherein said crystalline ion-association substance having the general formula (I) comprises a tetradentate borate complex anion selected from the group consisting of tetrakis(4-fluorophenyl) borate anion, tetrakis(4-fluorobiphenyl) borate anion, tetrakis[3,5-bis(trifluoromethyl)phenyl] borate anion, tetrakis(3,5-difluorophenyl) borate anion, tetrakis[4-(trifluoromethyl)phenyl] borate anion, tetrakis(2,3,5,6-tetrafluorophenyl) borate anion, tetrakis(1,2,3,4,5-pentafluorophenyl) borate anion, tetrakis(3,4,5-trifluorophenyl) borate anion, tetrakis(3-fluoropropane) borate anion, tetrakis[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl] borate anion, tetrakis(2,4,6-trifluorophenyl) borate anion, tetrakis(nonafluorobutyl) borate anion, tetrakis(perfluorohexyl) borate anion, tetrakis(perfluoropentyl) borate anion,

090043-0310
T07E20"8E406860

tetrakis(perfluorooctyl) borate anion, tetrakis(perfluoro-3-methylbutyl) borate anion, tetrakis(perfluoro-5-methylbutyl) borate anion, tetrakis(heptafluoropropyl) borate anion, tetrakis(3,5-dichlorophenyl) borate anion, tetrakis(4-chlorophenyl) borate anion, tetrakis(benzyl chloride) borate anion, tetrakis(chlorobenzyl) borate anion, tetrakis[2-(perfluorobutyl)ethyl] borate anion, tetrakis[2-(perfluorohexyl)ethyl] borate anion, tetrakis[2-(perfluorooctyl)ethyl] borate anion, tetrakis[2-(perfluoro-7-methylhexyl)ethyl] borate anion, tetrakis[2-(perfluoro-5-methylhexyl)ethyl] borate anion, tetrakis[2,2,3,3-tetrafluoropropyl] borate anion, tetrakis(1H,1H,5H-octafluoropentyl) borate anion, tetrakis(1H-perfluorohexyl) borate anion, tetrakis(1,1-difluoroethyl) borate anion, tetrakis[3,5-bis(trifluoromethyl)benzyl] borate anion, tetrakis[4-(trifluoromethyl)benzyl] borate anion, tetrakis(3,5,-difluorobenzyl) borate anion, tetrakis(4-fluorobenzyl) borate anion, tetrakis(4-ethoxyphenyl) borate anion, tetrakis(4-methoxyphenyl) borate anion, tetrakis(4,5-dimethoxyphenyl) borate anion, tetrakis(4-butylphenyl) borate anion, tetrakis(t-butylphenyl) borate anion, tetrakis(phenyl) borate anion, tetrakis(biphenyl) borate anion, tetrakis(terphenyl) borate anion, tetrakis(mesityl) borate anion, tetrakis(pentamethylphenyl) borate anion, tetrakis(3,5-dimethylphenyl) borate anion, tetrakis(cyclopropyl) borate anion, tetrakis(cyclobutyl) borate anion, tetrakis(cyclohexyl) borate anion, tetrakis(cyclopentyl) borate anion, tetrakis(cyclooctyl) borate anion and tetrakis(phenoxybutyl) borate anion.

IN THE ABSTRACT:

After the claims, please insert a page containing the Abstract Of The Disclosure, which is attached hereto as a separately typed page.

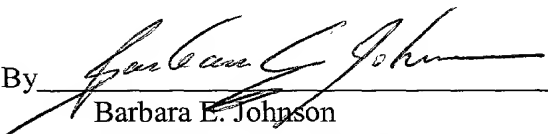
REMARKS

The specification has been amended to place the application in conformance with standard United States patent practice.

Examination and allowance of pending claims 16-23 are respectfully
requested.

Respectfully submitted,

WEBB ZIESENHEIM LOGSDON
ORKIN & HANSON, P.C.

By 

Barbara E. Johnson
Registration No. 31,198
Attorney for Applicant
700 Koppers Building
436 Seventh Avenue
Pittsburgh, PA 15219-1818
Telephone: 412-471-8815
Facsimile: 412-471-4094

09690433.03404

MARKED-UP AMENDED SPECIFICATION PARAGRAPHS

Page 1, first section heading

[Technical Field]

1. Field of the Invention

Page 1, second section heading

[Background of the Invention]

2. Description of the Related Art

Page 1, third complete paragraph

High molecular weight products produced by hardening (or polymerizing) the above-mentioned compounds have various uses, especially epoxy resin and silicone resin which have been widely used as adhesives, sealing, and paints in various fields such as automobile industry, housing/building material industry, civil engineering and construction industries, aircraft industry, and electric and electronic industries.

Page 1, fifth complete paragraph

It has been well known that the polymerization is generally carried out at room temperature or under heating [condition] conditions. Recently, [the] searches [on] for a photopolymerization catalyst or initiator have been conducted, because it may be preferable to carry out the polymerization under irradiation [condition dependently] conditions depending upon use. However, [any] no remarkable result has [not] been obtained.

Page 2, fourth complete paragraph

As [other] another example, the photopolymerization initiator disclosed in Japanese Patent Publication No. 62692/94 of the same applicant as this application can be cited. This [potopolymerization] photopolymerization initiator comprises a composite obtainable from a reaction between (a) charge transfer complex consisting of biscyclopentadienyl iron derivative and quinoid and (b) at least

one salt selected from a group consisting of tetrafluoroborates, hexafluorophosphates and hexafluoroantimonates.

Page 2, fifth complete paragraph:

On the contrary, regarding [to potopolymerization] the photopolymerization of organosiloxane, it is very hard to find [out the] an example. An example can be found only in Kevin D. Belfield et al., "Photoinitiated cationic ring-opening polymerization of a cyclosiloxane", Polymer Bulletin 38, pp. 165-168 (1997). [Kevin] Belfield et al. disclosed that when hexamethylene cyclotrisiloxane is exposed with U.V. light in the presence of sulfonium or iodonium salt or iminosulfonate derivative, it is subjected to a photo-initiating cationic ring-opening polymerization in solution or in the absence of solvent.

Paragraph bridging pages 2 and 3

Regarding [to] the thermal hardening (polymerization) reaction which is carried out at room temperature or under heating [condition] conditions, as example of catalyst for polymerization of epoxy compound, tertiary amine (such as benzylmethyl amine, [2,4,6-trisdimethylamine] 2,4,6-trisdimethylamine methylphenol, etc.), imidazole (such as 2-methylimidazole, 2-ethyl-4-methylimidazole, 2-heptadecylimidazole etc.), Lewis acid (such as BF_3 monoethylamine, BF_3 piperazine, etc.) have been known.

Page 3, first complete paragraph

The thermal hardening reaction of organosiloxane compound is [almost] classified into addition type and condensation type: in a reaction of the former type, peroxide or platinum compound is used as catalyst and in a reaction of the latter type, metal salt of carboxylic acid is used.

Page 3, second complete paragraph

As mentioned above, epoxy resins and silicone resins have been widely used. However, on producing the epoxy resins or silicone resins by hardening (or polymerizing) each monomer, the catalyst or initiator used in the thermal polymerization or photopolymerization of epoxy compound is completely different from that used in the thermal polymerization or photopolymerization of organosiloxane compound, and additionally, [the] an initiator for photopolymerization of organosiloxane compound [has not] is almost [been known] unknown.

Page 3, section heading

[Disclosure of the Invention]

Summary of the Invention

Page 4, section heading

[Best Mode for Carrying out the Invention] Description of the Preferred Embodiments

Page 4, third complete paragraph which begins with "The crystalline"

The crystalline ion-association substance of the present invention comprises, as [seeing] is seen from the general formula (I), a metallocene derivative cation and a tetradentate borate complex anion wherein the four ligands are the same to each other.

Paragraph bridging pages 4 and 5

In the general formula (I), the electron donative or electron attractive substituent is alkyl group, cycloalkyl group, aryl group, alkoxy group, silyl group, dialkyl group, acyl group, cycloalkenyl group, amino group, carboxyl group, [organobolyl] organoboranyl group, phosphino group, aldehyde group, hydroxyl group and the like. More particularly, the alkyl group is selected from among lower alkyl groups such as methyl group, ethyl group, propyl group and butyl group, or

pentyl group or amyl group; and the cycloalkyl group is selected from among cyclobutyl group, cyclopentyl group, cycloheptyl group, and cyclohexyl group. The aryl group is selected from among phenyl group, naphtyl group, etc.

Pages 8, first complete paragraph

The crystalline ion-association substance of the present invention contains a bulky ligand in the [cyclopentadienyl] cyclopentadienyl moiety of the metallocene derivative cation. Therefore, [the] a transition metal of the center nucleus [under] having a high oxidation state may maintain thermal stability, and the crystallinity between the metallocene derivative cation and the anion complex to be associated is synergistically increased.

Page 11, first complete paragraph

The crystalline ion-association substance of the present invention may have such a structure that one of four identical ligands of the borate complex anion is closed to the transition metal center of the metallocene derivative cation and is sandwiched between the two cyclopentadiene ligands of the metallocene derivative cation; the metallocene derivative cation per se having such a structure that the two cyclopentadiene ligands with various structure are positioned in the form of [dihederal] a dihedral structure with respect to the transition metal center.

Paragraph bridging pages 11 and 12

In photopolymerization of a cationically polymerizable organic substance, the polymerization initiator of the present invention is used in the amount of from 0.1 to 10 weight parts, preferably 0.5 to 4 weight parts with respect to 100 weight parts of the cationically polymerizable organic substance; when the cationically polymerizable organic substance absorbs usually 2000 to 9000 mJ/cm² of energy by irradiation with U.V. light having the wavelength of 200-700nm, basically

200-400nm, a high molecular weight polymer is produced. However, [the] an irradiation operation with more energy may be required depending upon the type of polymerizable substance. The irradiation can be carried out at any condition, that is, at ordinary temperature, under cooling condition, or under heating condition; and at atmospheric pressure or vacuum, or in the presence of inert gas.

Page 12, third complete paragraph

When compatibility between the cationically polymerizable organic substance and the polymerization initiator is poor, a suitable solvent such as hydrocarbon solvents, halogenated hydrocarbon solvents, alcoholic solvents, phenolic solvents, ether/acetal solvents, ketone solvents, ester solvents, nitrogen-containing compound solvents may be used. The concrete examples of the solvent are dichloromethane, chloroform, methanol, tetrahydrofuran, acetone, [metylethyl] methylethyl ketone, [acetonitorile] acetonitrile, etc. The solvent is used in 5-3 times amount with respect to 100 weight parts of the cationically polymerizable organic substance, that is, 500-300 weight parts.

Page 17, subparagraph III) (b)

(b) the hardened product has the substantially unchanged characteristics of the starting material itself; for example, when it is mixed with the [cationiacly] cationically polymerizable organic substance such as epoxy compound, the obtainable polymer product (hardened product) has the unchanged inherent characteristics of epoxy compound, and additionally, it is possible to produce composite product (hardened product) consisting of at least two cationically [polymeraizable] polymerizable organic substances which are of [the] a different type from each other.

Page 18, second paragraph

In preparation of the crystalline ion-association substance of the present invention, commercially available products (for example, products sold by Tokyo Chemicals Co. or [Aldolich] Aldrich Co.) can be used as metallocene derivative. Other metallocene derivatives can be prepared by the well-known methods for preparation disclosed in the following references:

Page 22, first complete paragraph

By using [the] a similar apparatus and procedure to those [ised] used in [the] Example 4, 0.46g of (dihydroxyboryl) ferrocenium/tetrakis(3,5-difluorophenyl) borate was obtained (yield 51%), starting from 0.3g of commercially available ferroceneboronic acid (CAS 12152-94-2), 0.021g of iron(III) chloride, 30ml of acetonitrile, 10ml of pure water and 0.635g of tetrakis (3,5-difluorophenyl) borate sodium salt.

Paragraph bridging pages 26 and 27

On the other hand, in case of using an organosiloxane compound having volatility and subliming property, a test sample was prepared as [follpws] follows:

In [the] a similar bottle to that described above, 10 weight parts of dichloroemethane is added with respect to 100 weight parts of the organosiloxane compound, and then the predetermined amount of polymerization initiator is added thereto. The resulting liquid mixture is stirred to disperse the initiator. Thereafter, the liquid mixture enclosed in the bottle is irradiated repeatedly with U.V. light ($6000\text{mJ}/\text{cm}^2$) four times from [outer] outside of the bottle. The obtained test sample (rubber-like hardened product produced in the bottle) is taken out and transferred to a glass cylinder for

Soxhlet extraction test (glass filter with filter plate No. GP-100) to measure gel fraction.

Page 32, second complete paragraph

To 100 weight parts of decamethylcyclopentasiloxane (D5) or [dodecamethylcyclohexasiloxane] dodecamethylcyclohexasiloxane (D6), 2 weight parts of each polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 8 or 10, 4 weight parts of benzophenone (sensitizer) and 30 weight parts of dichloromethane were added. The obtained mixture was stirred and mixed to prepare a solution in which the organosiloxane compound, the sensitizer and the polymerization initiator were homogeneously dissolved in the solvent. The obtained solution was fed to the center recess of the hole slide glass of one hole type without overflowing the solution from the recess. The hole slide glass was put into a hot air circulating oven and maintained at 60°C for 10 min. The test film was cooled to room temperature and irradiated with U.V. light (600 mJ/cm²). The gel fraction of the hardened films was reported in the following Table 4.

Page 33, second complete paragraph

To 100 weight parts of 1,3-bis(glycidoxypropyl) tetramethyldisiloxane (silicone-modified epoxy monomer) (Gelest Inc.; SIH1115.0; CAS 126-80-7), 1 weight part of each polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 2, 3, 8, 9, 10, 11, 12 or 13, 2 weight parts of benzophenone (sensitizer) and 50 weight parts of dichloromethane were added. The obtained mixture was stirred and mixed to prepare a solution in which the silicone-modified epoxy compound, the sensitizer and the polymerization initiator were homogeneously dissolved in the solvent. The obtained solution was fed to the

center recess of the hole slide glass of one hole type without overflowing the solution from the recess. The hole slide glass was put into a hot air circulating oven and maintained at 60°C for 10 min. and then at 80°C for 3 [mine] min. Each test film was irradiated with U.V. light (8000mJ/cm²).

Page 40, first complete paragraph

These examples show the fact that the polymerization initiator which comprises the crystalline ion-association substance prepared in the above-mentioned Example 3, 9, 11 or 12 has an ability to [proceed] produce a thermal polymerization of a mixture consisting of cyclic siloxane and epoxy compound.

Page 42, first complete paragraph beginning with "The polymerization"

The polymerization initiator of the present invention [have such a] has the unique property that it can initiate both photopolymerization and thermal polymerization when used in polymerizing cationically polymerizable organic substance, though the polymerization initiator comprises an identical crystalline ion-association substance.

Page 42, second complete paragraph beginning with "In particular"

In particular, since the photopolymerization initiator for organosiloxane has [not almost] been little developed, the polymerization initiator of the present invention is valuable.

Paragraph bridging pages 42 and 43

For the above-mentioned unique property of the polymerization initiator of the present invention, it is possible to obtain a merit in practical use; that is, after the U.V. light irradiation, it is possible to carry out the hardening in a shade zone which is not exposed to U.V. light or a deep zone to which U.V. light [dose] does not reach by means of heating (photopolymerization plus thermal

polymerization). This merit is very important, because, in accordance with conventional method, when the hardening is carried out by using both means of photopolymerization and thermal polymerization in accordance with conventional method, it is necessary to modify a monomer itself; for example, to prepare a modified organosiloxane having epoxy group.

Page 43, last complete paragraph

Therefor, it is possible to [spread] extend the field and method for use of cationically polymerizable organic substances by using the polymerization initiator of the present invention.

09600438-032404

NOVEL CRYSTALLINE ION-ASSOCIATION SUBSTANCE,
PROCESS FOR PRODUCING THE SAME, AND POLYMERIZATION
INITIATOR

ABSTRACT OF THE INVENTION

A polymerization initiator for cationically polymerizable organic substances which comprises a crystalline ion-association substance having such a unique property that it can initiate not only photopolymerization but thermal polymerization when used in polymerizing a cationically polymerizable organic substance. The crystalline ion-association substance is represented by the general formula (I): $[\{C_5(R^1)_n\}_{2m}M_m]^{1+}[\{B(R^2)_4\}^-]_1$.

090043-034
TUE 06/06/00

09/890438

Novel crystalline ion-association substance, Process for producing the same, and Polymerization initiator

Technical Field

The present invention relates to a novel crystalline ion-association substance, process for producing the same, and a polymerization initiator for cationically polymerizable organic substances which comprises said crystalline ion-association substance.

Background of the Invention

As the cationically polymerizable organic substances, many compounds have been well known such as methanol compounds, ethylene compounds, polyacetal compounds, organosiloxane compounds, polyamide compounds, heterocyclic compounds, etc.

High molecular products produced by hardening (or polymerizing) the above-mentioned compounds have various uses, especially epoxy resin and silicone resin have been widely used as adhesives, sealing, and paints in various fields such as automobile industry, housing/building material industry, civil engineering and construction industries, aircraft industry, and electric and electronic industries.

Cationic polymerization of epoxy compound or organosiloxane compound, which is a means for producing epoxy resin or silicone resin, is carried out in the presence of polymerization catalyst or polymerization initiator.

It has been well known that the polymerization is generally carried out at room temperature or under heating condition. Recently, the searches on photopolymerization catalyst or initiator have been conducted, because it may be preferable to carry out the polymerization under irradiation condition dependently upon use. However, any remarkable result has not been obtained.

Regarding photopolymerization of epoxy compound, the example of initiator for cationic photopolymerization is onium salt which contains element having lone pair to which proton or other cation compound is bonded via coordinate bond. Typical example of the onium salt is aromatic diazonium salt, aromatic iodonium salt, and aromatic sulfonium salt. Many of the onium salts contain halogen metal complex anion (BF_4^- , PF_6^- ,

AsF₆⁻, SbF₆⁻, etc.) as counter ion.

The working mechanism of these conventional photopolymerization initiators such as diazonium salt, iodium salt, and sulfonium salt is as follows: At first, Brønsted acid is produced by U.V. light irradiation. Then, the produced Brønsted acid reacts with the cationically polymerizable organic substances and molecular chain of polymer grows.

Another example of photopolymerization initiator is salt of metallocene complex. In this case, Lewis acid is produced as active species by U.V. light irradiation, and insertion of monomer occurs at the Lewis acid, whereby molecular chain of polymer grows.

Photopolymerization initiator containing borate counter anion has been disclosed in Japanese Patent Laid-open Nos. 143,044/87 and 182,701/90. In accordance with these literatures, the working mechanism is as follows: When dyestuff which is cation component of the complex is exposed to U.V. light, it is excited to singlet state; it receives electron from the borate salt which is anion component; then the produced borate radical dissociates one of the ligands to generate a radical, whereby the radical polymerization proceeds.

As other example, the photopolymerization initiator disclosed in Japanese Patent Publication No. 62692/94 of the same applicant as this application can be cited. This photopolymerization initiator comprises a composite obtainable from a reaction between (a) charge transfer complex consisting of biscyclopentadienyl iron derivative and quinoid and (b) at least one salt selected from a group consisting of tetrafluoroborates, hexafluorophosphates and hexafluoroantimonates.

On the contrary, regarding to photopolymerization of organosiloxane, it is very hard to find out the example. An example can be found only in Kevin D. Belfield et al., "Photoinitiated cationic ring-opening polymerization of a cyclosiloxane", Polymer Bulletin 38, pp. 165-168 (1997). Kevin et al. disclosed that when hexamethylene cyclotrisiloxane is exposed with U.V. light in the presence of sulfonium or iodonium salt or iminosulfonate derivative, it is subjected to photo-initiating cationic ring-opening polymerization in solution or in the absence of solvent.

Regarding to thermal hardening (polymerization) reaction which is

0360433 073101

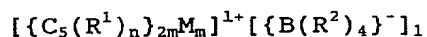
carried out at room temperature or under heating condition, as example of catalyst for polymerization of epoxy compound, tertiary amine (such as benzylmethyl amine, 2,4,6-trisdimethylamine methylphenol, etc.), imidazole (such as 2-methylimidazole, 2-ethyl-4-methylimidazole, 2-heptadecylimidazole etc.), Lewis acid (such as BF_3 , monoethylamine, BF_3 piperazine, etc.) have been known.

The thermal hardening reaction of organosiloxane compound is almost classified into addition type and condensation type: in reaction of the former type, peroxide or platinum compound is used as catalyst and in reaction of the latter type, metal salt of carboxylic acid is used.

As mentioned above, epoxy resins and silicone resins have been widely used. However, on producing the epoxy resins or silicone resins by hardening (or polymerizing) each monomer, the catalyst or initiator used in the thermal polymerization or photopolymerization of epoxy compound is completely different from that used in the thermal polymerization or photopolymerization of organosiloxane compound, and additionally, the initiator for photopolymerization of organosiloxane compound has not almost been known.

Disclosure of the Invention

The inventor has newly developed a crystalline ion-association substance having a general formula (I);



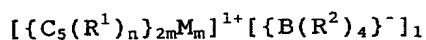
wherein M is a transition metal of center nucleus; C_5 is cyclopentadienyl group; R^1 is electron donative or electron attractive substituent bonded to a carbon atom of cyclopentadienyl group, or an organic group bridging two neighboring carbon atoms; \underline{n} is in the range of 0 to 3; \underline{m} is either 1 or 2; $\underline{1}$ is either 1 or 2; R^2 is a ligand coordinated to boron atom (B), and the four R^2 (s) are the same to each other.

It has also been found that this ion-association substance has an unique characteristics; that is, it has an ability to initiate not only photopolymerization but thermal polymerization of cationically polymerizable organic substances, especially both of epoxy compound and organosiloxane compound.

Therefore, the primary object of the present invention is to provide the novel crystalline ion-association substance having the

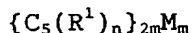
above-mentioned general formula (I).

The secondary object of the present invention is a polymerization initiator for cationically polymerizable organic materials, characterized in that said polymerization initiator comprises the crystalline ion-association substance having the general formula (I);

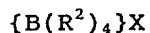


wherein M is a transition metal of center nucleus; C₅ is cyclopentadienyl group; R¹ is an electron donative or electron attractive substituent bonded to a carbon atom of cyclopentadienyl group, or an organic group bridging two neighboring carbon atoms; n is in the range of 0 to 3; m is either 1 or 2; 1 is either 1 or 2; R² is a ligand coordinated to boron atom (B), and the four R²(s) are the same to each other.

Also, the third object of the present invention is a method of producing the novel crystalline ion-association substance having the above-mentioned formula (I), characterized in that metallocene derivative of mono- or di-nucleus structure having a general formula (II);



wherein M, C₅, R¹, m and n have the same meaning as mentioned above, is reacted with a tetradentate borate complex compound having a general formula (III);



wherein R² has the same meaning as mentioned above and X is an alkali metal atom.

Best Mode for Carrying out the Invention

The crystalline ion-association substance of the present invention comprises, as seen from the general formula (I), metallocene derivative cation and tetradentate borate complex anion wherein the four ligands are the same to each other.

In the general formula (I), the electron donative or electron attractive substituent is alkyl group, cycloalkyl group, aryl group, alkoxy group, silyl group, dialkyl group, acyl group, cycloalkenyl group, amino group, carboxyl group, organobolyl group, phosphino group, aldehyde group, hydroxyl group and the like. More particularly, the alkyl group is selected from among lower alkyl groups such as methyl group, ethyl group,

The organic group bonding two neighboring carbon atoms is alkylene group such as polyacetylene group, polymethylene group $[-(\text{CH}=\text{CH})_n-$, $-(\text{CH}_2)_n-$: $n = 2$ to 6], etc.

Also, the metallocene derivative cation which constitutes the crystalline ion-association substance having the general formula (I) may be metallocenophane cation having mono-nucleus structure wherein the substituent on one cyclopentadienyl is bonded to the substituent on another cyclopentadienyl within one molecule; or dimetallocene cation having di-nucleus structure wherein the substituent on one of cyclopentadienyl within one molecule is bonded to the substituent on cyclopentadienyl within other molecule; or indenyl group having organic group bridging two neighboring carbon atoms.

The specific examples of the above-mentioned metallocene derivative cation are acetyl ferrocenium, tert.-amyl ferrocenium, benzoyl ferrocenium, n-butyl ferrocenium, cyclohexenyl ferrocenium, cyclopentenyl ferrocenium, 1,1'-diacetyl ferrocenium, 1,1'-di-n-butyl ferrocenium, N,N-dimethylaminomethyl ferrocenium, 1,1'-dimethyl ferrocenium, ethyl ferrocenium, (dihydroxyboranyl) ferrocenium, 1-hydroxyethyl ferrocenium, hydroxymethyl ferrocenium, vinyl ferrocenium, 1,1-bis(diphenylphosphino) ferrocenium, ferrocenium, t-butyl ferrocenium, dibutyl ferrocenium, bis(cyclopentadienyl) chromium cation, bis(cyclopentadienyl) molybdenum chloride cation, bis(cyclopentadienyl) osmium cation, bis(t-butylcyclopentadienyl)

titanium chloride cation, bis(cyclopentadienyl) dicarbonyl titanium cation, bis(cyclopentadienyl) titanium chloride cation, bis(cyclopentadienyl) tungsten chloride cation, bis(i-propylcyclopentadienyl) tungsten chloride cation, vanadocenium, bis(n-butylcyclopentadienyl) zirconium chloride cation, bis(t-butylcyclopentadienyl) zirconium chloride cation, bis(cyclopentadienyl) zirconium chloride cation, bis(ethylcyclopentadienyl) zirconium chloride cation, bis(methylcyclopentadienyl) zirconium chloride cation, bis(indenyl) dimethyl zirconium cation, bis(t-butylcyclopentadienyl) hafnium chloride cation, bis(ethylcyclopentadienyl) hafnium chloride cation, bis(iso-propylcyclopentadienyl) hafnium chloride cation, diferrocenium derivative cation, etc.

On the other hand, the counter anion of the crystalline ion-association substance of the present invention is tetradentate borate complex anion $[B(R^2)_4]^-$. In the formula, R^2 is a ligand coordinated to boron atom (B) of the center nucleus and is selected from among aryl group, halogenated aryl group, halogen haloform aryl group, cycloalkynyl group, halogenated cycloalkyl group, halogenated cycloalkynyl group, cycloalkyloxy group, cycloalkenyloxy group, alkadienyl group, alkatrienyl group, alkynyl group, halogenated alkenyl group, halogenated alkadienyl group, halogenated alkatrienyl group, halogenated alkynyl group, heterocyclic group, etc., but the four ligands (R^2) are the same to each other. Also, the two adjacent ligands may chemically bond to each other to form two rings bonding the ligands within one borate complex anion.

Embodiments of the tetranentate borate complex anion are tetrakis(4-fluorophenyl) borate anion, tetrakis(4-fluorobiphenyl) borate anion, tetrakis[3,5-bis(trifluoromethyl)phenyl] borate anion, tetrakis(3,5-difluorophenyl) borate anion, tetrakis[4-(trifluoromethyl)phenyl] borate anion, tetrakis(2,3,5,6-tetrafluorophenyl) borate anion, tetrakis(1,2,3,4,5-pentafluorophenyl) borate anion, tetrakis(3,4,5-trifluorophenyl) borate anion, tetrakis(3-fluoropropane) borate anion, tetrakis[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl]

borate anion, tetrakis(2,4,6-trifluorophenyl) borate anion,
 tetrakis(nonafluorobutyl) borate anion, tetrakis(perfluorohexyl)
 borate anion, tetrakis(perfluoropentyl) borate anion,
 tetrakis(perfluorooctyl) borate anion, tetrakis
 (perfluoro-3-methylbutyl) borate anion,
 tetrakis(perfluoro-5-methylbutyl) borate anion,
 tetrakis(heptafluoropropyl) borate anion,
 tetrakis(3,5-dichlorophenyl) borate anion, tetrakis(4-chlorophenyl)
 borate anion, tetrakis(benzyl chloride) borate anion,
 tetrakis(chlorobenzyl) borate anion,
 tetrakis[2-(perfluorobutyl)ethyl] borate anion,
 tetrakis[2-(perfluorohexyl)ethyl] borate anion,
 tetrakis[2-(perfluorooctyl)ethyl] borate anion,
 tetrakis[2-(perfluoro-7-methyloctyl)ethyl] borate anion,
 tetrakis[2-(perfluoro-5-methylhexyl)ethyl] borate anion,
 tetrakis(2,2,3,3-tetrafluoropropyl) borate anion,
 tetrakis(1H,1H,5H-octafluoropentyl) borate anion,
 tetrakis(1H-perfluorohexyl) borate anion, tetrakis(1,1-difluoroethyl)
 borate anion, tetrakis[3,5-bis(trifluoromethyl)benzyl] borate anion,
 tetrakis[4-(trifluoromethyl)benzyl] borate anion,
 tetrakis(3,5,-difluorobenzyl) borate anion, tetrakis(4-fluorobenzyl)
 borate anion, tetrakis(4-ethoxyphenyl) borate anion,
 tetrakis(4-methoxyphenyl) borate anion, tetrakis(4,5-dimethoxyphenyl)
 borate anion, tetrakis(4-butylphenyl) borate anion,
 tetrakis(t-butylphenyl) borate anion, tetrakis(phenyl) borate anion,
 tetrakis(biphenyl) borate anion, tetrakis(terphenyl) borate anion,
 tetrakis(mesityl) borate anion, tetrakis(pentamethylphenyl) borate
 anion, tetrakis(3,5-dimethylphenyl) borate anion,
 tetrakis(cyclopropyl) borate anion, tetrakis(cyclobutyl) borate anion,
 tetrakis(cyclohexyl) borate anion, tetrakis(cyclopentyl) borate anion,
 tetrakis(cyclooctyl) borate anion, tetrakis(phenoxybutyl) borate anion,
 etc.

Preferably are tetrakis(4-fluorophenyl) borate anion,
 tetrakis[3,5-bis(trifluoromethyl)phenyl] borate anion,
 tetrakis(3,5-difluorophenyl) borate anion,

056043 0740

tetrakis[4-(trifluoromethyl)phenyl] borate anion,
 tetrakis[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl]
 borate anion, tetrakis(4-chlorophenyl) borate anion,
 tetrakis(3,5-dichlorophenyl) borate anion,
 tetrakis[2-(perfluorobutyl)ethyl] borate anion,
 tetrakis(4-fluorobiphenyl) borate anion, and
 tetrakis(1,2,3,4,5-pentafluorophenyl) borate anion.

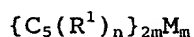
The crystalline ion-association substance of the present invention contains bulky ligand in cyclopentadienyl moiety of the metallocene derivative cation. Therefore, the transition metal of center nucleus under high oxidation state may maintain thermal stability, and the crystallinity between the metallocene derivative cation and the anion complex to be associated is synergistically increased.

The borate complex anion is composed of boron atom and four identical ligands which are situated at tetrahedral positions around the boron center. The ligand has side chain groups. Accordingly, the external factor to induce decomposition of the anion, such as attack by active compounds and/or atom, may be sterically inhibited similarly to the metallocene derivative cation. Also the electron attractive substituent such as halogen, etc., is introduced into the side chain of the ligand, therefore the electron density of the carbon atom attached to boron atom is decreased. Whereby, the boron atom center is protected from the external attack.

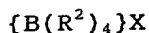
As a result, the crystalline ion-association substance of the present invention is highly stable when preserving alone or in the form of a mixture with the cationically polymerizable organic substance and possibly various additives.

Now, a method of producing the present crystalline ion-association substance having the general formula (I) will be explained.

The crystalline ion-association substance is produced by reacting metallocene derivative having the general formula (II);



wherein M, C_5 , R^1 , \underline{m} , and \underline{n} have the same meaning as mentioned above, with tetradentate borate complex compound having the general formula (III);



wherein B and R^2 have the same meanings as mentioned above, and X is alkali metal atom.

The reaction between the metallocene derivative and the borate complex compound is carried out in an acidic solvent at the molar ratio of metallocene derivative to borate complex compound of 1:1 in case of monometallocene or of 1:2 in case of dimetallocene and at the temperature ranging from ordinary temperature to 100°C, preferably from ordinary temperature to 60°C.

The usable acidic solvent is 3-50% aqueous solution of sulfuric acid, preferably 5-20% aqueous solution of sulfuric acid.

In case of using metal salt, the reaction is carried out in mixed solvent between pure water and organic solvent at the temperature ranging from 0 to 100°C, preferably from ordinary temperature to 70°C with using oxidizing agent (electron scavenger) such as $FeCl_3$, etc., at the ratio of 1:0.1-1, preferably 1:0.1-0.3 with respect to the metallocene derivative.

As the organic solvent, an aprotic solvent is preferable. For example, acetone, acetonitrile, or the like is used.

The mixing ratio between organic solvent and pure water is 1:0.1-1, preferably 1:0.1-0.5.

As other methods for production, an electrode oxidation method in a polar solvent may be used.

The examples of the crystalline ion-association substance produced by the aforesaid reaction are ferrocenium/tetrakis(3,5-difluorophenyl) borate, dimethyl ferrocenium/tetrakis(3,5-difluorophenyl) borate, 1,2,4,1',2',4'-hexamethyl ferrocenium/tetrakis(3,5-difluorophenyl) borate, n-butyl ferrocenium/tetrakis(3,5-difluorophenyl) borate, tert.-amyl ferrocenium/tetrakis(3,5-difluorophenyl) borate, ferroceneboronic acid/tetrakis(3,5-difluorophenyl) borate, dihydroxyboranyl ferrocenium/tetrakis(3,5-difluorophenyl) borate, ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate, dimethyl ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate, 1,2,4,1',2',4'-hexamethylphenyl ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate,

dimethyl ferrocenium/tetrakis(pentafluorophenyl) borate,
1,2,4,1',2',4'-hexamethyl ferrocenium/tetrakis(pentafluorophenyl)
borate, 1,2,4,1',2',4'-hexamethyl
ferrocenium/tetrakis[4-(trifluoromethyl)phenyl] borate,
1,2-diferrocenylethyl
ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate,
ferrocenium/tetrakis(3,5-difluorophenyl) borate,
ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate,
ferrocenium/tetrakis(2,3,5,6-tetrafluorophenyl) borate,
ferrocenium/tetrakis(1,2,3,4,5-pentafluorophenyl) borate,
ferrocenium/tetrakis[4-(trifluoromethyl)phenyl] borate,
ferrocenium/tetrakis(4-fluorophenyl) borate,
ferrocenium/tetrakis(3,4,5-trifluorophenyl) borate, dimethyl
ferrocenium/tetrakis(3,5-difluorophenyl) borate, dimethyl
ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate,
dimethyl ferrocenium/tetrakis(2,3,5,6-tetrafluorophenyl) borate,
dimethyl ferrocenium/tetrakis(1,2,3,4,5-pentafluorophenyl) borate,
dimethyl ferrocenium/tetrakis[4-(trifluoromethyl)phenyl] borate,
dimethyl ferrocenium/tetrakis(4-fluorophenyl) borate, dimethyl
ferrocenium/tetrakis(3,4,5-trifluorophenyl) borate, tetramethyl
ferrocenium/tetrakis(3,5-difluorophenyl) borate, tetramethyl
ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate,
tetramethyl ferrocenium/tetrakis(2,3,5,6-tetrafluorophenyl) borate,
tetramethyl ferrocenium/tetrakis(1,2,3,4,5-pentafluorophenyl) borate,
tetramethyl ferrocenium/tetrakis[4-(trifluoromethyl)phenyl] borate,
tetramethyl ferrocenium/tetrakis(4-fluorophenyl) borate, tetramethyl
ferrocenium/tetrakis(3,4,5-trifluorophenyl) borate, hexamethyl
ferrocenium/tetrakis(3,5-difluorophenyl) borate, hexamethyl
ferrocenium/tetrakis[3,5-bis(trifluoro)phenyl] borate, hexamethyl
ferrocenium/tetrakis(2,3,5,6-tetrafluorophenyl) borate, hexamethyl
ferrocenium/tetrakis(1,2,3,4,5-pentafluorophenyl) borate, hexamethyl
ferrocenium/tetrakis[4-(trifluoromethyl)phenyl] borate, hexamethyl
ferrocenium/tetrakis(4-fluorophenyl) borate, hexamethyl
ferrocenium/tetrakis(3,4,5-trifluorophenyl) borate, n-butyl
ferrocenium/tetrakis(3,5-difluorophenyl) borate, n-butyl ferrocenium/

tetrakis[3,5-bis(trifluoromethyl)phenyl] borate, n-butyl ferrocenium/tetrakis(2,3,5,6-tetrafluorophenyl) borate, n-butyl ferrocenium/tetrakis(1,2,3,4,5-pentafluorophenyl) borate, n-butyl ferrocenium/tetrakis[4-(trifluoromethyl)phenyl] borate, n-butyl ferrocenium/tetrakis(4-fluorophenyl) borate, n-butyl ferrocenium/tetrakis(3,4,5-trifluorophenyl) borate, tert.-amyl ferrocenium/tetrakis(3,5-difluorophenyl) borate, tert.-amyl ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate, tert.-amyl ferrocenium/tetrakis(2,3,5,6-tetrafluorophenyl) borate, tert.-amyl ferrocenium/tetrakis(1,2,3,4,5-pentafluorophenyl) borate, tert.-amyl ferrocenium/tetrakis[4-(trifluoromethyl)phenyl] borate, tert.-amyl ferrocenium/tetrakis(4-fluorophenyl) borate, and tert.-amyl ferrocenium/tetrakis(3,4,5-trifluorophenyl) borate.

The crystalline ion-association substance of the present invention may have such a structure that one of four identical ligands of the borate complex anion is closed to the transition metal center of the metallocene derivative cation and is sandwiched between the two cyclopentadiene ligands of the metallocene derivative cation; the metallocene derivative cation per se having such a structure that the two cyclopentadiene ligands with various structure are positioned in the form of dihedral structure with respect to the transition metal center.

In case that the ligand of the anion complex is a substituted phenyl group, in comparison with ligand having substituent only at para-position, ligand having two substituents at 3- and 5-position enters to the deeper position between two cyclopentadiene ligands of the cation, and the transition metal center of the cation is sandwiched by the two substituents of the ligand of the anion, whereby the ion-association substance having higher crystallinity is produced.

The polymerization initiator for cationically polymerizable organic substance which comprises the crystalline ion-association substance having the general formula (I) has an ability to initiate not only photopolymerization but thermal polymerization, as well as thermal polymerization plus photopolymerization.

In photopolymerization of cationically polymerizable organic substance, the polymerization initiator of the present invention is used

in the amount of from 0.1 to 10 weight parts, preferably 0.5 to 4 weight parts with respect to 100 weight parts of the cationically polymerizable organic substance; when the cationically polymerizable organic substance absorbs usually 2000 to 9000 mJ/cm² of energy by irradiation with U.V. light having the wavelength of 200-700nm, basically 200-400nm, a high molecular polymer is produced. However, the irradiation operation with more energy may be required depending upon the type of polymerizable substance. The irradiation can be carried out at any condition, that is, at ordinary temperature, under cooling condition, or under heating condition; and at atmospheric pressure or vacuum, or in the presence of inert gas.

In case of photopolymerization plus thermal polymerization, after the photopolymerization is carried out under the above-mentioned condition, the un-reacted substance or the obtained polymer having low polymerization degree is heated at 70-200°C for 10 min. to 1 hour, preferably at 100-160°C for 10-30 min., whereby, polymer product with high molecular weight is be produced.

In case of thermal polymerization, the polymerization initiator of the present invention is used in the amount of 0.1-10 weight parts, preferably 0.5-4 weight parts with respect to 100 weight parts of the cationically polymerizable organic substance. The cationically polymerizable organic substance is heated at 70-200°C for 10 min. to 2 hours, preferably at 140-180°C for 30-90min. to produce polymer product with high molecular weight.

When compatibility between the cationically polymerizable organic substance and the polymerization initiator is poor, a suitable solvent such as hydrocarbon solvents, halogenated hydrocarbon solvents, alcoholic solvents, phenolic solvents, ether/acetal solvents, ketone solvents, ester solvents, nitrogen-containing compound solvents may be used. The concrete examples of the solvent are dichloromethane, chloroform, methanol, tetrahydrofuran, acetone, metylethyl ketone, acetonitorile, etc. The solvent is used in 5-3 times amount with respect to 100 weight parts of the cationically polymerizable organic substance, that is, 500-300 weight parts.

It is also possible to add sensitizer to the reaction system in the

Alternatively, in case of using visible ray, conventional dyestuff type sensitizers such as coumarins, thiazines, azines, acridines, and xanthenes may be used.

The sensitizer is used in the amount of 0.1-10 weight parts, preferably 0.5-5 weight parts with respect to the 100 weight parts of the cationically

polymerizable organic substance.

The examples of cationically polymerizable organic substances that can be polymerized with the polymerization initiator of the present invention are methylol compounds, ethylene unsaturated compounds, polyacetal compounds, organosiloxane compounds, polyamide compounds, and heterocyclic compounds. Generally, cellulose compounds, unsaturated polyesters, polystyrenes, methacrylic and acrylic compounds, polyimides, polycarbonates, polyesterimides, polyamideimides, etc. can be used.

For example, compounds which have, as functional group, cyclic ether group containing more than two carbon atoms and one oxygen atom, especially, epoxy compounds having cyclic ether group of three-members ring type are effective.

Some typical examples of epoxy compound are monoepoxy compounds such as olefin oxide, butylglycidylether, styrene oxide, phenylglycidylether and p-alkylphenolglycidyl ether which may be used as reactive diluent; polyepoxide compounds having at least two cyclic ether groups of three-members ring type in side chain and at chain terminal within one molecule, such as, for example, cresol-novolak type epoxy compound, phenol-novolak type epoxy compound, bisphenol A type epoxy compound, bisphenol F type epoxy compound, and alicyclic epoxy compounds, etc. Also, their hydrolysis products or halogenation products such as fluorinated or brominated type compounds may be used.

Monooxetane compound having cyclic ether group of four-members ring type, and oxetane compound having more than two cyclic ether groups of four-members ring type within one molecule are also effective.

The polymerization initiator of the present invention is also effective for polymerization of organosiloxane compounds, especially cyclic siloxanes. Oligomers containing cyclic siloxane group in molecule, at terminal or as pendant group are also effective.

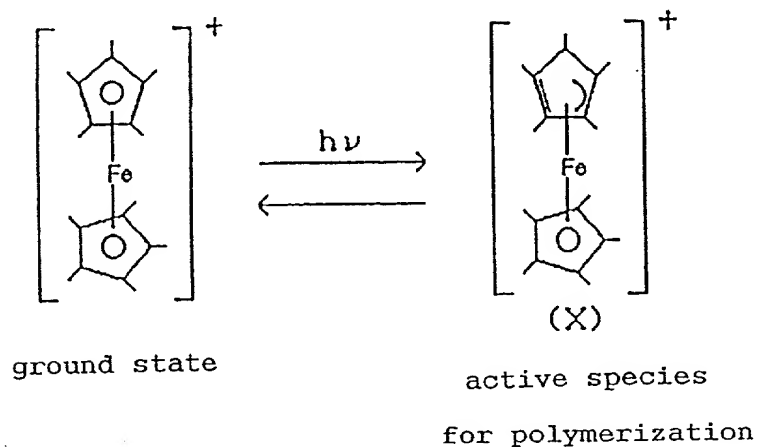
It is possible to use at least two cationically polymerizable organic substances in the form of mixture. The term "at least two substances" means not only a mixture consisting of two or more substances which are of the same type as each other but also a mixture consisting of two or more substances which are of different type from each other, such as,

Although the reaction mechanism in polymerization of cationically polymerizable organic substance using the polymerization initiator of the present invention has not been fully clarified, it is presumed as follows.

The fact that the coordination mode of cyclopentadienyl ligand changes depending on a condition has been observed in many organometallic complexes (for example, J.M. O'Connor, C.P. Casey, Chem. Rev. 87, p.307~318 (1987)).

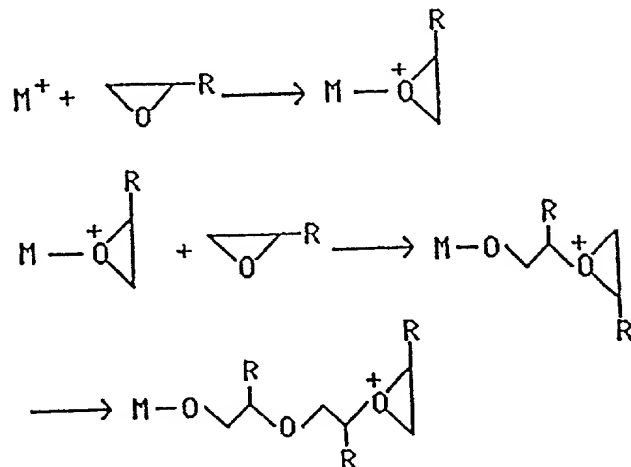
In the absence of a monomer, the active species (X) is returned to the original ground state again. As a result, under U.V. light irradiation or heating, an equilibrium mixture of the original ground state and the active species (X) is formed. In the presence of a monomer, however, the ferricenium cation moiety in the active species (X), with small degree of steric hinderance around Fe atom, initiates a polymerization at the Fe center of the cation moiety, and causes propagation of the polymer chain by repeated insertion of monomer.

Presumable Reaction Mechanism



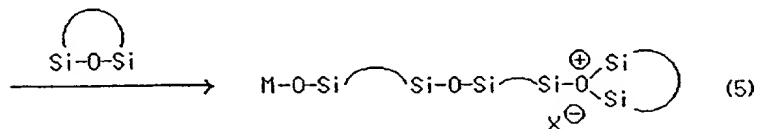
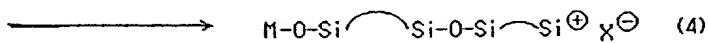
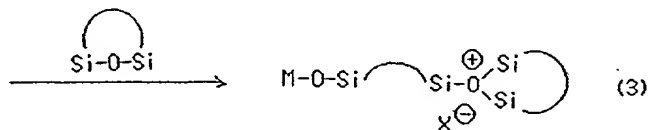
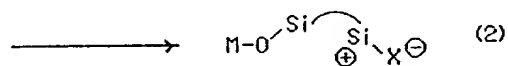
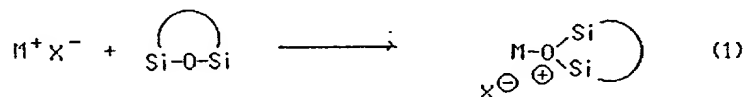
Polymerization Reaction of Epoxy Compound

(M is a center metal of active species)



Polymerization Reaction of Organosiloxane compound

(M is a center metal of active species)



On the other hand, though the polymerization reaction is partly halted by a chain transfer and so on, the U.V. light irradiation or heating keeps generating the active species (X) by the photo- or thermal excitation. The produced active species initiates polymerization. Thus, under irradiation with U.V. light or heating, the continuous transformation of monomer to polymer occurs, but cutting-off of U.V. light or heating stops generation of new active species for polymerization reaction. Therefore, when the existing active species is exhausted, the polymerization itself terminates.

The polymerization initiator of the present invention has the following characteristics;

- I) when the initiator exists alone,
 - (a) it is highly resistant to heat, moisture (water) and acid and alkali;
 - (b) it has good compatibility with cationically polymerizable organic substances such as epoxy compound;
- II) when the initiator exists in the form of a mixture with the cationically polymerizable organic substances,
 - (a) it has an ability to harden thick film even when it is used in the small amount (0.5-4%);
 - (b) it is not subjected to a decomposition by the moisture (water) in the mixture;
 - (c) it has good stability in viscosity of the mixture, and
- III) as to the characteristics of the hardened product produced by photopolymerization, thermal polymerization, or photopolymerization plus thermal polymerization,
 - (a) the hardened product has no electrolytic corrosion, for example, it shows great anti-electrolytic corrosion toward copper strip;
 - (b) the hardened product has the substantially unchanged characteristics of the starting material itself; for example, when it is mixed with the cationically polymerizable organic substance such as epoxy compound, the obtainable polymer product (hardened product) has the unchanged inherent characteristics of epoxy compound, and additionally, it is

possible to produce composite product (hardened product) consisting of at least two cationically polymerizable organic substances which are of the different type from each other.

Now, the invention will be explained in more detail with the following examples; however these examples are intended to illustrate the invention and are not to be construed to limit the scope of the invention.

In preparation of the crystalline ion-association substance of the present invention, commercially available products (for example, products sold by Tokyo Chemicals Co. or Aldolich Co.) can be used as metallocene derivative. Other metallocene derivatives can be prepared by the well-known methods for preparation disclosed in the following references:

a) precursors;

- L. DeVRIES, J. Org. Chem., 25 1838 (1960)
- R.S. THRELKEL, J.E. BERCAW., J. Organometallic Chemistry, 136 1-5 (1977)
- D. FEITLER, G.M. WHITESIDES., Inorg. Chem. Vol.15, No.2, 466 (1976)

b) metallocene derivatives;

- D.M. DUGGAN, D.N. HENDRICKSON., Inorg. Chem. Vol.14, No.5, 955 (1975)
- KAI-MING, J.C. CALABRESE, W.M. BEIFF, J.S. MILLER., Organometallics, 10 688-693 (1991)

Also, among the tetradentate borate complex compounds, as tetrakis[3,5-bis(trifluoromethyl)phenyl] borate sodium salt and tetrakis(1,2,3,4,5-pentafluorophenyl) borate lithium salt, commercially available products sold by DOJIN CHEMICALS Co. and Asahi Glass Co., Ltd., respectively, can be used; but, for example, tetrakis(3,5-difluorophenyl) borate complex compound may be prepared as described in the following reference example.

Reference Example

Synthesis of tetrakis(3,5-difluorophenyl) borate sodium salt

A dried flask made of Pyrex glass (capacity: 500ml) provided with a reflux condenser was charged with inert gas to purge the air from the flask. Then, metallic magnesium (4.65g) and anhydrous diethyl ether (100ml) were fed to the flask, and the resulting solution was stirred

and cooled by ice bath. A solution prepared separately by adding anhydrous diethyl ether (50ml) to 1-bromo-3,5-difluorobenzene (43.52g) was dropped thereto for an hour, and the resulting solution was left still for three hours. At the end of the reaction, a liquid containing boron trifluoride ether complex (4.542g) in anhydrous diethyl ether was dropped during 40 minutes, and left still for 16 hours with stirring at the room temperature. Then, an aqueous solution of sodium carbonate (30g) in pure water (100ml) was dropped during 30 minutes. After the solution was kept stirring at the room temperature for 24 hours, the water phase and the organic phase were separated from each other. The separated organic phase was dried with sodium sulfate and filtered; the filtrate was put into an evaporator (oil bath temperature: 70°C); and diethyl ether was evaporated, thereby obtaining a liver-brown colored solid.

The liver-brown colored solid was further purified with silica gel, and white solid of tetrakis(3,5-difluorophenyl) borate sodium salt (10.3g) was obtained.

The following literatures were referred.

- H. KOBAYASHI, T. SONODA, Y. INUKAI, K. TAKUMA., Technical Reports of ASAHI GLASS CO., LTD., 42 (1983)
- J. ICHIKAWA, H. KOBAYASHI, T. SONODA., Organic Synthetic Chemistry, 46, 943~953 (1988)
- K. FUKUI, M. KASHIWAGI, H. MIYAMOTO, A. SONODA, J. ICHIKAWA, H. KOBAYASHI, T. SONODA., J. Fluorine Chem., 57, 307~321 (1992)

Example 1

Synthesis of ferrocenium/tetrakis(3,5-difluorophenyl) borate

In a dried eggplant-type flask made of Pyrex glass (capacity: 300ml) provided with a magnetic stirrer, 1g of commercially available ferrocene (CAS 102-54-5) was added to 10g of conc. sulfuric acid. The resulting solution was stirred at room temperature for 5 hours, and then 100ml of pure water was gradually added thereto. The flask containing the solution was cooled, and the solution was filtered with PTFE filter paper.

The filtrate was transferred to a beaker made of Pyrex glass (capacity: 300ml), and ethanol solution (5ml) containing 2.75g of tetrakis(3,5-difluorophenyl) borate sodium salt was added thereto with stirring by a magnetic stirrer. Blue colored crystal precipitated.

The precipitate was filtered, washed with pure water, dried by evaporator, washed with toluene, and dried again by evaporator.

1.6g of ferrocenium/tetrakis(3,5-difluorophenyl) borate was obtained (yield 43%).

Example 2

Synthesis of diamethyl ferrocenium/tetrakis(3,5-difluorophenyl) borate

In the similar apparatus to that used in Example 1, 1g of commercially available dimethyl ferrocene (CAS 1291-47-0) was added to 10g of conc. sulfuric acid. The resulting solution was stirred at room temperature for 16 hours, and then 100ml of pure water was added thereto. The flask containing the solution was cooled, and the solution was filtered with PTFE filter paper.

The filtrate was transferred to a beaker made of Pyrex glass (capacity: 300ml), and ethanol solution (5ml) containing 2.38g of tetrakis(3,5-difluorophenyl) borate sodium salt was added with stirring by a magnetic stirrer. Blue colored crystal precipitated.

The precipitate was filtered, washed with pure water, dried by evaporator, washed with toluene, and dried again by evaporator.

1.68g of dimethyl ferrocene/tetrakis(3,5-difluorophenyl) borate was obtained (yield 53%).

The identification of the obtained substance was carried out by ^1H -NMR analysis (Nuclear Magnetic Resonance Equipment EX-400, NEC Co.), and the following data was obtained.

^1H NMR [25°C, deuterated acetone, chemical shift of peak(ppm)]:

3.20 (cyclopentadienyl); 6.0-8.0 (phenyl)

Example 3

Synthesis of 1,2,4,1',2',4'-hexamethyl ferrocenium/tetrakis(3,5-difluorophenyl) borate

In the similar apparatus to that used in Example 1, 1g of 1,2,4,1',2',4'-hexamethyl ferrocene was added to 15g of conc. sulfuric acid. The resulting solution was stirred at room temperature for 16 hours, and then 100ml of pure water was added thereto. The flask containing the solution was cooled, and the solution was filtered with PTFE filter paper. The filtrate was heated to 60°C by water bath with stirring, and

ethanol solution (5ml) containing 1.89g of tetrakis(3,5-difluorophenyl) borate sodium salt was added. Blue-green colored crystal precipitated.

The precipitate was filtered, washed with pure water, dried by evaporator, washed with toluene, and dried again by evaporator.

1.29g of 1,2,4,1',2',4'-hexamethyl ferrocenium/tetrakis(3,5-difluorophenyl) borate was obtained (yield 47.5%).

Example 4

Synthesis of n-butyl ferrocenium/tetrakis(3,5-difluorophenyl) borate

To an eggplant-type flask made of Pyrex glass (capacity: 100ml) provided with a magnetic stirrer, 0.32g of iron(III) chloride and 30ml of acetonitrile were fed and iron(III) chloride was dissolved into acetonitrile. Furthermore, 0.48g of commercially available n-butyl ferrocene (CAS 31904-29-7) and 20ml of pure water were added thereto, and the resulting solution was stirred for 1 hour. Then, 0.97g of tetrakis(3,5-difluorophenyl) borate sodium salt was added thereto. The resulting solution was heated to 60°C by water bath with stirring and left still for 30 min. Thereafter, water and organic solvent of the reaction solution were distilled out by evaporator. To the obtained residue, dichloromethane and pure water were added, and the solution was stirred for 30min. Then, the water phase and the organic phase were separated from each other. The water phase was introduced into evaporator to remove the solvent. The obtained residue was dried, washed with toluene, and dried again by evaporator.

1g of n-butyl ferrocenium/tetrakis(3,5-difluorophenyl) borate was obtained (yield 71.5%).

The identification was carried out by ¹H-NMR analysis similarly to the Example 2, and the following data was obtained.

¹H-NMR [25°C, deuterated acetone, chemical shift of peak(ppm)]:

3.15 (dicyclopentadienyl); 6.71, 6.47 (phenyl); 0.86-2.04 (butyl)

Example 5

Synthesis of tert.-amyl ferrocenium/tetrakis(3,5-difluorophenyl) borate

By using the similar apparatus and procedure to those used in the Example 4, 0.87g of tert.-amyl ferrocenium/tetrakis(3,5-difluorophenyl)

0000438-073101

borate was obtained (yield 60.7%), starting from 0.51g of commercially available tert.-amyl ferrocene (CAS 53954-86-2), 0.32g of iron(III) chloride, 30ml of acetonitrile, 20ml of pure water and 0.97g of tetrakis(3,5-difluorophenyl) borate sodium salt.

¹HNMR [25°C, deuterated acetone, chemical shift of peak(ppm)]:

32.1 (cyclopentadienyl); 12.82 (methylene); 6.72, 6.48 (phenyl); -12.1 (methyl(amy1))

Example 6

Synthesis of (dihydroxyboryl)

ferrocenium/tetrakis(3,5-difluorophenyl) borate

By using the similar apparatus and procedure to those used in the Example 4, 0.46g of (dihydroxyboryl)

ferrocenium/tetrakis(3,5-difluorophenyl) borate was obtained (yield 51%), starting from 0.3g of commercially available ferroceneboronic acid (CAS 12152-94-2), 0.021g of iron(III) chloride, 30ml of acetonitrile, 10ml of pure water and 0.635g of tetrakis(3,5-difluorophenyl) borate sodium salt.

The identification was carried out by ¹H-NMR analysis similarly to the Example 2, and the following data was obtained.

¹HNMR [25°C, deuterated acetone, chemical shift of peak(ppm)]:

32.6 (cyclopentadienyl); 6.72, 6.44 (phenyl)

Example 7

Synthesis of ferrocenium/tetrakis[3,5-bis(trifluoromethyl) phenyl] borate

In the similar apparatus to that used in Example 1, 0.5g of commercially available ferrocene was added to 10g of conc. sulfuric acid. The resulting solution was stirred at room temperature for 5 hours, and then 100ml of pure water was added thereto. The flask containing the solution was cooled, and the solution was filtered with PTFE filter paper. The filtrate was transferred to a beaker made of Pyrex glass (capacity: 300ml), and ethanol solution (7ml) containing 2.48g of tetrakis[3,5-bis(trifluoromethyl)phenyl] borate sodium salt (CAS 79060-88-1) was added. Blue colored crystal precipitated.

The precipitate was filtered, washed with pure water, dried by evaporator, washed with toluene, and dried again by evaporator.

T01E20" B240660

1.73g of ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate was obtained (yield 61.3%).

Example 8

Synthesis of dimethyl ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate

By using the similar apparatus and procedure to those used in the Example 1, 1.36g of dimethyl ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate was obtained (yield 54.1%), starting from 0.5g of dimethyl ferrocene, 10g of conc. sulfuric acid, and ethanol solution (7ml) containing 2.15g of tetrakis[3,5-bis(trifluoromethyl)phenyl] borate sodium salt.

The identification was carried out by $^1\text{H-NMR}$ analysis similarly to the Example 2, and the following data was obtained.

$^1\text{HNMR}$ [25°C, deuterated acetone, chemical shift of peak(ppm)]:

34.5, 31.2 (cyclopentadienyl); 7.78, 7.67 (phenyl); -10.63 (methyl)

Example 9

Synthesis of 1,2,4,1',2',4'-hexamethyl ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate

In the similar apparatus to that used in Example 1, 0.5g of 1,2,4,1',2',4'-hexamethyl ferrocene was added to 10g of conc. sulfuric acid. The resulting solution was stirred at room temperature for 16 hours, and then 100ml of pure water was added thereto. The flask containing the solution was cooled, and the solution was filtered with PTFE filter paper. The filtrate was heated to 60°C by water bath with stirring, and ethanol solution (7ml) containing 1.71g of tetrakis[3,5-bis(trifluoromethyl)phenyl] borate sodium salt was added. Blue-green colored crystal precipitated.

The precipitate was filtered, washed with pure water, dried by evaporator, washed with toluene, and dried again by evaporator.

1.08g of 1,2,4,1',2',4'-hexamethyl ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate was obtained (yield 51.5%).

The identification was carried out by $^1\text{H-NMR}$ analysis similarly to the Example 2, and the following data was obtained.

$^1\text{HNMR}$ [25°C, deuterated acetone, chemical shift of peak(ppm)]:

17.1 (methyl); 7.58, 7.50 (phenyl)

Example 10

Synthesis of dimethyl ferrocenium/tetrakis(pentafluorophenyl) borate

In the similar apparatus to that used in Example 1, 0.5g of dimethyl ferrocene was added to 10g of conc. sulfuric acid. The resulting solution was stirred at room temperature for 5 hours, and then 100ml of pure water was added thereto. The flask containing the solution was cooled, and the solution was filtered with PTFE filter paper. The filtrate was heated to 40°C by water bath with stirring, and ethanol solution (7ml) containing 1.6g of tetrakis(pentafluorophenyl) borate sodium salt (CAS 2797-28-6) was added. Blue colored crystal precipitated.

The precipitate was filtered, washed with pure water, dried by evaporator, washed with toluene, and dried again by evaporator.

0.97g of dimethyl ferrocenium/tetrakis(pentafluorophenyl) borate was obtained (yield 46.5%).

The identification was carried out by ¹H-NMR analysis similarly to the Example 2, and the following data was obtained.

¹HNMR [25°C, deuterated acetone, chemical shift of peak(ppm)]:

34.0 (methyl); 7.10, 7.02 (phenyl)

Example 11

Synthesis of 1,2,4,1',2',4'-hexamethyl ferrocenium/tetrakis(pentafluorophenyl) borate

In the similar apparatus to that used in Example 1, 0.5g of 1,2,4,1',2',4'-hexamethyl ferrocene was added to 10g of conc. sulfuric acid. The resulting solution was stirred at room temperature for 16 hours, and then 100ml of pure water was added thereto. The flask containing the solution was cooled, and the solution was filtered with PTFE filter paper. The filtrate was heated to 60°C by water bath with stirring, and ethanol solution (7ml) containing 1.27g of tetrakis(pentafluorophenyl) borate sodium salt was added. Blue-green colored crystal precipitated.

The precipitate was filtered, washed with pure water, dried by evaporator, washed with toluene, and dried again by evaporator.

1.05g of 1,2,4,1',2',4'-hexamethyl ferrocenium/tetrakis(pentafluorophenyl) borate was obtained (yield 60%).

The identification was carried out by ^1H -NMR analysis similarly to the Example 2, and the following data was obtained.

^1H NMR [25°C, deuterated acetone, chemical shift of peak(ppm)]:

34.0 (methyl)

Example 12

Synthesis of 1,2,4,1',2',4'-hexamethyl ferrocenium/tetrakis[4-(trifluoromethyl)phenyl] borate

In the similar apparatus to that used in Example 1, 0.5g of 1,2,4,1',2',4'-hexamethyl ferrocene was added to 10g of conc. sulfuric acid. The resulting solution was stirred at room temperature for 16 hours, and then 100ml of pure water was added thereto. The flask containing the solution was cooled, and the solution was filtered with PTFE filter paper. The filtrate was heated to 60°C by water bath with stirring, and ethanol solution (5ml) containing 1.14g of tetrakis[4-(trifluoromethyl)phenyl] borate sodium salt was added. Blue-green colored crystal precipitated.

The precipitate was filtered, washed with pure water, dried by evaporator, washed with toluene, and dried again by evaporator.

0.71g of 1,2,4,1',2',4'-hexamethyl ferrocenium/tetrakis[4-(trifluoromethyl)phenyl] borate was obtained (yield 44.7%).

Example 13

Synthesis of (2-ferrocenylethyl) ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate

In the similar apparatus to that used in Example 1, 1g of commercially available 1,2-diferrocenyl ethane (CAS 12156-05-7) was added to 15g of conc. sulfuric acid. The resulting solution was stirred at room temperature for 16 hours, and then 100ml of pure water was added thereto. The flask containing the solution was cooled, and the solution was filtered with PTFE filter paper. The filtrate was heated to 70°C by water bath with stirring, and 4.86g of tetrakis[3,5-bis(trifluoromethyl)phenyl] borate sodium salt was added. Blue-green colored crystal precipitated. After the flask was left still for 1 hour under stirring, the precipitate was filtered, washed with pure water, dried by evaporator, washed with toluene, and dried again by evaporator.

3.16g of (2-ferrocenylethyl) ferrocenium/tetrakis[3,5-bis(trifluoromethyl)phenyl] borate was obtained (yield 59.2%).

The identification was carried out by $^1\text{H-NMR}$ analysis similarly to the Example 2, and the following data was obtained.

$^1\text{HNMR}$ [25°C, deuterated acetone, chemical shift of peak(ppm)]:
16.6 (methylene); 7.57, 7.43 (phenyl)

In order to verify the fact that the crystalline ion-association substances prepared in the above-mentioned Examples 1-13 can act as a polymerization initiator which has an ability to polymerize cationically polymerizable organic substances by means of U.V. light irradiation, heating, or U.V. light irradiation plus heating to produce polymer with highmolecular weight (hardened product), some experiments were conducted. The detail of the experiments will be disclosed in the following Examples.

In the examples, a reaction system comprising organosiloxane (cationically polymerizable organic substance) and polymerization initiator was prepared by the following method; To a clear glass bottle with threaded mouth (capacity: 10ml), a polymerization initiator comprising the crystalline ion-association substance prepared in the Examples 1-13 is fed in the amount of 2 weight parts with respect to 100 weight parts of organosiloxane. After 10-50 weight parts of dichloromethane is further added thereto as medium for dispersing the initiator, the resulting mixture is stirred to disperse fully the initiator in the reaction system.

In case of using an organosiloxane compound having low volatility among organosiloxanes, a test sample was prepared as follows: The solution prepared in accordance with the above-mentioned procedure is fed to a center recess in a hole slide glass of one hole type without overflowing the solution from the recess. The hole slide glass is put into a hot air circulating oven and maintained at 60°C for 10 min. and then at 80°C for 3 min. Finally the temperature of the test sample is put back to room temperature.

On the other hand, in case of using an organosiloxane compound having volatility and subliming property, a test sample was prepared as follows:

In the similar bottle to that described above, 10 weight parts of dichloromethane is added with respect to 100 weight parts of the organosiloxane compound, and then the predetermined amount of polymerization initiator is added thereto. The resulting liquid mixture is stirred to disperse the initiator. Thereafter, the liquid mixture enclosed in the bottle is irradiated repeatedly with U.V. light ($6000\text{mJ}/\text{cm}^2$) four times from outer of the bottle. The obtained test sample (rubber-like hardened product produced in the bottle) is taken out and transferred to a glass cylinder for Soxhlet extraction test (glass filter with filter plate No. GP-100) to measure gel fraction.

The irradiation operation is carried out by using U.V. light from a metal halide lamp provided with a cold mirror. The exposure amount is determined as integrating luminous energy of light having the wavelength of 365nm.

The heating operation is carried out by maintaining the flask containing the reaction system under the atmosphere whose temperature is previously set up at the predetermined point (160°C or 180°C) in a thermostat.

The gel fraction is determined by putting the hardened product which is produced on the slide glass plate or in the glass bottle into Soxhlet extractor; extracting ingredient with low molecular weight from the hardened product for 16 hours; taking out the hardened product; drying the hardened product at 80°C in a hot air circulation oven for 1 hour; and measuring the weight of un-extracted ingredient of the hardened product.

The stirring and mixing operation of organosiloxane compound, polymerization initiator and solvent is carried out at room temperature by a hand homogenizer with 5mm of generator diameter, a small shaker, or the like.

Examples 14-26

To 100 weight parts of 1,3,5,7-tetramethylcyclotetrasiloxane (Gelest Inc., USA; SIT 7530.0; CAS 2370-88-9), 2 weight parts of each polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 1-13 and 50 weight parts of dichloromethane were added. The obtained mixture was stirred and mixed to prepare solution in which the organosiloxane compound and

the polymerization initiator were homogeneously dissolved in the solvent. The obtained solution was fed to the center recess of the hole slide glass of one hole type without overflowing the solution from the recess. The hole slide glass was put into hot air circulating oven and maintained at 60°C for 10 min. and then at 80°C for 3 min. Each test film was irradiated with U.V. light (8000 mJ/cm²).

The gel fraction of the hardened film was reported in Table 1.

Table 1

<u>Example No.</u>	<u>Initiator</u>	<u>Gel fraction of hardened film (%)</u>
14	Example 1	76.2
15	Example 2	68.4
16	Example 3	35.6
17	Example 4	61.0
18	Example 5	28.9
19	Example 6	79.3
20	Example 7	49.0
21	Example 8	77.5
22	Example 9	38.8
23	Example 10	89.3
24	Example 11	53.5
25	Example 12	40.6
26	Example 13	77.2

Examples 27-30

In a clear glass bottle with threaded mouth, 2 weight parts of each polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 8, 9, 10 or 11, 4 weight parts of benzophenone (CAS 119-61-9) (sensitizer) and 30 weight parts of dichloromethane were added to 100 weight parts of hexamethylcyclotetrasiloxane (D3) (Gelest Inc.; SIH 6105.0; CAS 541-05-9). The obtained mixture was stirred and mixed to prepare reaction system through which the polymerization initiator was homogeneously dispersed. The reaction system kept within the bottle was irradiated directly with U.V. light (6000 mJ/cm²) four times. The rubber-like

hardened product produced in the bottle was taken out and transferred to the glass cylinder for Soxhlet extraction to measure gel fraction.

The gel fraction of the hardened product was reported in Table 2.

Table 2

<u>Example No.</u>	<u>Initiator</u>	<u>Gel fraction of hardened product (%)</u>
27	Example 8	60.8
28	Example 9	43.5
29	Example 10	77.8
30	Example 11	51.4

Example 31

In a clear glass bottle with threaded mouth, 2 weight parts of the polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 10, 4 weight parts of benzophenone (sensitizer) and 30 weight parts of dichloromethane were added to 100 weight parts of octamethylcyclotetrasiloxane (D4)(Gelest Inc.; SIO 6700.0; CAS 556-67-2). The obtained mixture was stirred and mixed to prepare reaction system through which the polymerization initiator was homogeneously dispersed. The reaction system kept within the bottle was irradiated directly with U.V. light (6000mJ/cm²) four times. The rubber-like hardened product produced in the bottle was taken out and transferred to the glass cylinder for Soxhlet extraction to measure the gel fraction.

The hardened product showed the gel fraction of 69.3%.

Example 32

To 100 weight parts of decamethylcyclopentasiloxane (D5)(Shin-Etsu Chemical Co., Ltd.; LS 9000; CAS 541-02-6), 2 weight parts of polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 10, 4 weight parts of benzophenone (sensitizer) and 50 weight parts of dichloromethane were added. The obtained mixture was stirred and mixed to prepare solution in which the organosiloxane compound and the polymerization initiator were homogeneously dissolved in the solvent. The obtained solution was fed to the center recess of the hole slide glass of one hole type without

overflowing the solution from the recess. The hole slide glass was put into a hot air circulating oven and maintained at 60°C for 10 min. and then at 80°C for 3 min. The test film was irradiated with U.V. light (8000mJ/cm²).

The hardened film showed the gel fraction of 70.7%.

Example 33

To 100 weight parts of dodecamethylcyclotetrasiloxane (D6)(Shin-Etsu Chemical Co., Ltd.; LS 9060; CAS 540-97-6), 2 weight parts of polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 10, 4 weight parts of benzophenone (sensitizer) and 50 weight parts of dichloromethane were added. The obtained mixture was stirred and mixed to prepare solution in which the organosiloxane compound and the polymerization initiator were homogeneously dissolved in the solvent. The obtained solution was fed to the center recess of the hole slide glass of one hole type without overflowing the solution from the recess. The hole slide glass was put into a hot air circulating oven and maintained at 60°C for 10 min. and then at 80°C for 3 min. The test film was irradiated with U.V. light (8000mJ/cm²).

The hardened film showed the gel fraction of 52.4%.

Examples 34-36

To 100 weight parts of 2,2,5,5-tetramethyl-2,5-disilano-1-oxacyclopentane (Gelest Inc.; SIT 7540.0; CAS 7418-20-4), 2 weight parts of each polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 8, 10 or 11, 4 weight parts of benzophenone (sensitizer) and 50 weight parts of dichloromethane were added. The obtained mixture was stirred and mixed to prepare solution in which the organosiloxane compound, the sensitizer and the polymerization initiator were homogeneously dissolved in the solvent. The obtained solution was fed to the center recess of the hole slide glass of one hole type without overflowing the solution from the recess. The hole slide glass was put into a hot air circulating oven and maintained at 60°C for 10 min. and then at 80°C for 3 min. Each test film was irradiated with U.V. light (8000mJ/cm²).

The gel fraction of the hardened film was reported in Table 3.

Table 3

<u>Example No.</u>	<u>Initiator</u>	<u>Gel fraction of hardened film (%)</u>
34	Example 8	36.3
35	Example 10	72.4
36	Example 11	35.2

Example 37

To 100 weight parts of hexaethylcyclotrisiloxane (Gelest Inc.; SIH 5990.0; CAS 2031-79-0), 2 weight parts of polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 10, 4 weight parts of benzophenone (sensitizer) and 50 weight parts of dichloromethane were added. The obtained mixture was stirred and mixed to prepare solution in which the organosiloxane compound, the sensitizer and the polymerization initiator were homogeneously dissolved in the solvent. The obtained solution was fed to the center recess of the hole slide glass of one hole type without overflowing the solution from the recess. The hole slide glass was put into a hot air circulating oven and maintained at 60°C for 10 min. and then at 80°C for 3 min. The test film was irradiated with U.V. light (8000mJ/cm²).

The hardened film showed the gel fraction of 40.2%.

Example 38

To 100 weight parts of phenylhydrocyclosiloxane (Gelest Inc.; SIP 6736.5), 2 weight parts of polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 10, 4 weight parts of benzophenone (sensitizer) and 50 weight parts of dichloromethane were added. The obtained mixture was stirred and mixed to prepare solution in which the organosiloxane compound, the sensitizer and the polymerization initiator were homogeneously dissolved in the solvent. The obtained solution was fed to the center recess of the hole slide glass of one hole type without overflowing the solution from the recess. The hole slide glass was put into a hot air circulating oven and maintained at 60°C for 10 min. The test film was irradiated with U.V. light (8000mJ/cm²).

The hardened film showed the gel fraction of 65.8%.

In order to verify the fact that the polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 8 or 10 is effective in photopolymerization plus thermal polymerization of organosiloxane compound (cyclic siloxane), some hardening tests will be disclosed in the following Examples 39-46.

Examples 39-42

To 100 weight parts of decamethylcyclopentasiloxane (D5) or dodecamethylcyclohexasiloxane (D6), 2 weight parts of each polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 8 or 10, 4 weight parts of benzophenone (sensitizer) and 30 weight parts of dichloromethane were added. The obtained mixture was stirred and mixed to prepare solution in which the organosiloxane compound, the sensitizer and the polymerization initiator were homogeneously dissolved in the solvent. The obtained solution was fed to the center recess of the hole slide glass of one hole type without overflowing the solution from the recess. The hole slide glass was put into a hot air circulating oven and maintained at 60°C for 10 min. The test film was cooled to room temperature and irradiated with U.V. light (6000mJ/cm²). The gel fraction of the hardened films was reported in the following Table 4.

Then, the test film irradiated with U.V. light (6000mJ/cm²) as mentioned above was subjected to thermal treatment by maintaining the film under atmosphere whose temperature was pre-set at 160°C for 1 hour. The gel fraction of the obtained test films was reported in the following Table 5.

Table 4

Example No.	Cyclic siloxane	Initiator	Gel fraction of hardened film (%)
39	D5	Example 8	53.2
40	D6	Example 8	38.4
41	D5	Example 10	59.6
42	D6	Example 10	43.4

Table 5

<u>Example No.</u>	<u>Gel fraction (%)</u>
39	79.4
40	82.3
41	91.2
42	89.5

In order to verify the fact that the polymerization initiator of the present invention is effective also in polymerization of the so-called modified silicone compound, said silicone compound having siloxane group in its main chain and cationically polymerizable functional group at terminal (or in its side chain), some hardening tests will be disclosed in the following Examples 43-50.

Examples 43-50

To 100 weight parts of 1,3-bis(glycidoxypropyl) tetramethyldisiloxane (silicone-modified epoxy monomer) (Gelest Inc.; SIH 1115.0; CAS 126-80-7), 1 weight part of each polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 2, 3, 8, 9, 10, 11, 12 or 13, 2 weight parts of benzophenone (sensitizer) and 50 weight parts of dichloromethane were added. The obtained mixture was stirred and mixed to prepare solution in which the silicone-modified epoxy compound, the sensitizer and the polymerization initiator were homogeneously dissolved in the solvent. The obtained solution was fed to the center recess of the hole slide glass of one hole type without overflowing the solution from the recess. The hole slide glass was put into a hot air circulating oven and maintained at 60°C for 10 min. and then at 80°C for 3 mine. Each test film was irradiated with U.V. light (8000mJ/cm²).

The gel fraction of the hardened films was reported in the Table 6.

Table 6

<u>Example No.</u>	<u>Initiator</u>	<u>Gel fraction of hardened film (%)</u>
43	Example 2	70.6
44	Example 3	57.6

45	Example 8	84.4
46	Example 9	73.5
47	Example 10	77.9
48	Example 11	75.2
49	Example 12	48.3
50	Example 13	85.0

In order to verify the fact that the polymerization initiator which comprises the crystalline ion-association substance prepared in the above-mentioned Example 3, 9, 11 or 12 has an ability to carry out the hardening by three means; U.V. light irradiation, U.V. light irradiation plus heating and heating only, some hardening tests were disclosed in the following Examples 51-85.

In the hardening tests, an epoxy compound was used which is a typical cationically polymerizable organic substance.

Example 51-62

These examples relate to hardening by means of U.V. light irradiation.

Epoxy compound selected from among phenol-novolak type epoxy compound [epoxy equivalence of 170-190; DAINIPPON INK & CHEMICALS, Inc.; EPICRON (registered trademark) N-730A], bisphenol F type epoxy compound [epoxy equivalence of 165-185; DAINIPPON INK & CHEMICALS, Inc.; EPICRON (registered trademark) 830] and hydrogenated bisphenol A type epoxy compound [epoxy equivalence of 215; Petrochemical Shell Epoxy Co., Ltd.; EPICOAT (registered trademark) RXE 21] was dissolved in methyl ethyl ketone in such amount that the solution has the solid content of 50%. To the obtained solution, the polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 3, 9, 11 or 12 was added in the amount of 1 weight part in case that the polymerization initiator comprises the crystalline ion-association substance prepared in the Example 3 or 12, or of 0.7 weight part in case of the polymerization initiator which comprises the crystalline ion-association substance prepared in the Example 9 or 11, with respect to 100 weight parts of the epoxy compound. Two weight parts of dibenzosuberone (sensitizer) (CAS 1210-35-1) was also added thereto. Then, the obtained mixture was stirred and mixed to prepare solution in which

the epoxy compound, the sensitizer and the polymerization initiator were homogeneously dissolved in the solvent. The solution was applied to surface of glass plate at the uniform thickness (as dry film) of 200 μ m. The glass plate was put into a 60°C hot air circulating oven for 20 min. to remove the solvent. Finally, the film was dried by maintaining in the hot air circulating oven at 80°C for another 10 min. The obtained film was used as a test piece.

The irradiation operation was carried out by using U.V. light generated by a metal halide lamp provided with a cold mirror. The exposure amount was determined as integrating luminous energy of light having the wavelength of 365nm.

In order to determine the degree of hardening, the gel fraction of the film was measured. In the measurement of gel fraction, the test piece of hardened epoxy resin film which was obtained by hardening the epoxy compound on the glass plate was put into Soxhlet extractor. The extraction was carried out for 16 hours by using acetone as solvent to remove ingredient with low molecular weight. Then, the test piece was taken out from the extractor, put into a 80°C hot air circulating oven, and dried by maintaining in the oven for 1 hour. Thereafter, the weight of un-extracted ingredient of the test piece was measured.

Each test piece was irradiated with U.V. light at the exposure amount of 8000mJ/cm².

The gel fraction of the hardened film was reported in Table 7.

Table 7

Ex. No.	Epoxy compound	Initiator	Gel fraction(%)
51	phenol-novolak type	Ex. 3	85.3
52	ditto	Ex. 9	90.1
53	ditto	Ex.11	93.2
54	ditto	Ex.12	79.4
55	bisphenol F type	Ex. 3	83.5
56	ditto	Ex. 9	89.3
57	ditto	Ex.11	91.5
58	ditto	Ex.12	92.8
59	hydrogenated bisphenol A type	Ex. 3	83.6

60	ditto	Ex. 9	91.3
61	ditto	Ex.11	93.0
62	ditto	Ex.12	89.7

Examples 63-74

These examples relate to hardening by means of U.V. light irradiation plus heating.

The test pieces prepared from epoxy compounds in accordance with the same procedure to that used in the Example 51 were irradiated with U.V. light ($3000\text{mJ}/\text{cm}^2$). The gel fraction of the irradiated test pieces were reported in the following Table 8.

Then, the test pieces irradiated with U.V. light ($3000\text{mJ}/\text{cm}^2$) as mentioned above were subjected to thermal treatment by maintaining the test pieces under atmosphere whose temperature was pre-set at 160°C for 1 hour. The gel fraction of the obtained hardened products was reported in the following Table 9.

Table 8

<u>Ex. No.</u>	<u>Epoxy compound</u>	<u>Initiator</u>	<u>Gel fraction(%)</u>
63	phenol-novolak type	Ex. 3	62.3
64	ditto	Ex. 9	69.1
65	ditto	Ex.11	75.7
66	ditto	Ex.12	56.2
67	bisphenol F type	Ex. 3	70.3
68	ditto	Ex. 9	77.9
69	ditto	Ex.11	80.5
70	ditto	Ex.12	79.2
71	hydrogenated bisphnol A type	Ex. 3	76.7
72	ditto	Ex. 9	79.2
73	ditto	Ex.11	83.4
74	ditto	Ex.12	81.6

Table 9

<u>Example No.</u>	<u>Gel fraction (%)</u>
63	92.3

64	95.2
65	94.3
66	91.5
67	94.8
68	96.2
69	93.3
70	94.7
71	94.8
72	96.7
73	91.3
74	90.6

Examples 75-86

These examples show the fact that the polymerization initiator of the present invention is effective for thermal polymerization of epoxy compound.

The test pieces prepared in accordance with the same procedure to that used in the Example 51 were subjected to thermal treatment by maintaining each test piece under atmosphere whose temperature was pre-set at 180°C for 2 hours in a thermostat, without U.V. light irradiation. The gel fraction of the obtained hardened products was reported in Table 10.

Table 10

Ex. No.	Epoxy compound	Initiator	Gel fraction(%)
75	phenol-novolak type	Ex. 3	78.5
76	ditto	Ex. 9	80.9
77	ditto	Ex. 11	76.3
78	ditto	Ex. 12	85.7
79	bisphenol F type	Ex. 3	77.9
80	ditto	Ex. 9	79.1
81	ditto	Ex. 11	78.8
82	ditto	Ex. 12	69.2
83	hydrogenated bisphenol A type	Ex. 3	87.7
84	ditto	Ex. 9	93.1

85	ditto	Ex.11	91.3
86	ditto	Ex.12	92.1

The following examples show the fact that the polymerization initiators of the present invention have an ability to carry out hardening of a mixture which comprises cationically polymerizable substances of heterogeneous type by three means; U.V. light irradiation, U.V. light irradiation plus heating and heating.

Example 87-99

Hardening of mixture consisting of cyclic siloxane and hydrogenated bisphenol A epoxy resin

To a mixture consisting of 50 weight parts of dodecamethylcyclhexasiloxane (D6) and 50 weight parts of hydrogenated bisphenol A epoxy compound, 1 weight parts of each polymerization initiator which comprises the crystalline ion-association substance prepared in the above-mentioned Examples 1-13 and then 2 weight parts of dibenzosuberone (sensitizer) and 20 weight parts of dichloromethane were added. The obtained mixture was stirred and mixed to prepare solution in which the polymerizable substances, the sensitizer and the polymerization initiator were homogeneously dissolved in the solvent. The solution was applied to surface of glass plate at the uniform thickness (as dry film) of 200 μ m. In order to remove the solvent, the obtained film was maintained in a hot air circulating oven at 60°C for 10 minutes and then at 80°C for 3 minutes. The obtained film was irradiated with U.V. light (8000mJ/cm²).

The gel fraction of the hardened film is reported in Table 11.

Table 11

<u>Example No.</u>	<u>Initiator</u>	<u>Gel fraction of hardened film (%)</u>
87	Example 1	87.4
88	Example 2	81.5
89	Example 3	79.3
90	Example 4	88.7
91	Example 5	69.4
92	Example 6	77.9

93	Example 7	92.8
94	Example 8	89.7
95	Example 9	93.5
96	Example 10	91.4
97	Example 11	82.3
98	Example 12	76.4
99	Example 13	81.7

In order to verify the fact that the polymerization initiator which comprises the crystalline ion-association substance prepared in the above-mentioned Example 3, 9, 11 or 12 has an ability to proceed the polymerization (hardening) of mixture consisting of cyclic siloxane and epoxy resin by heating after U.V. light irradiation, some hardening tests were disclosed in the following Examples 100-107. The gel fraction of the obtained hardened products were reported in Tables 12 and 13.

Examples 100-107

In accordance with the same procedure to that used in the Example 87, test pieces were prepared starting from mixture consisting of dodecamethylcyclohexasiloxane (D6)(cyclic siloxane) and hydrogenated bisphenol A type epoxy compound. Each test piece was irradiated with U.V. light ($2000\text{mJ}/\text{cm}^2$). The gel fraction of the irradiated test piece was reported in the following Table 12. Then, the irradiated test piece was subjected to thermal treatment by maintaining each test piece in a hot air circulating oven whose temperature was pre-set at 160°C for 1 hour. The gel fraction of the obtained hardened product (film) was reported in the following Table 13.

Table 12

<u>Example No.</u>	<u>Initiator</u>	<u>Gel fraction of hardened film (%)</u>
100	Example 3	38.2
101	Example 9	50.1
102	Example 11	55.3
103	Example 12	39.2

Table 13

<u>Example No.</u>	<u>Initiator</u>	<u>Gel fraction of hardened film (%)</u>
104	Example 3	82.5
105	Example 9	91.3
106	Example 11	90.7
107	Example 12	88.1

Examples 108-111

These examples show the fact that the polymerization initiator which comprises the crystalline ion-association substance prepared in the above-mentioned Example 3, 9, 11 or 12 has an ability to proceed a thermal polymerization of mixture consisting of cyclic siloxane and epoxy compound.

By using the same starting materials and procedure to those used in the Example 87, test pieces were prepared. Each test piece was subjected to thermal treatment by maintaining the test piece in a hot air circulating oven whose temperature was pre-set at 180°C for 2 hours. The gel fraction of the obtained hardened product (film) was reported in Table 14.

Table 14

<u>Example No.</u>	<u>Initiator</u>	<u>Gel fraction of hardened film (%)</u>
108	Example 3	65.7
109	Example 9	85.7
110	Example 11	81.4
111	Example 12	73.1

Examples 112-135

The cationically polymerizable organic substance was irradiated with U.V. light in the presence of the polymerization initiator which comprises the crystalline ion-association substance prepared in the above-mentioned Example 3, 9, 11 or 12. The thickness of the obtained hardened film was reported in the following Table 15. Then, the hardened film obtained by U.V. light irradiation was subjected to thermal treatment. The gel fraction of the obtained hardened product was reported in the following Table 16.

The solution was prepared by dissolving each epoxy compound selected

0360438-0744
JUL 20 1966

from among phenol-novolak type epoxy compound, bisphenol F type epoxy compound and hydrogenated bisphenol A type epoxy compound in methyl ethyl ketone in such amount that the solution has the solid content of 97%. To the obtained solution, the polymerization initiator was added in the amount of 1 weight part in case that the polymerization initiator comprises the crystalline ion-association substance prepared in the Example 3 or 12, and of 0.7 weight part in case that the polymerization initiator comprises the crystalline ion-association substance prepared in the Example 9 or 11, with respect to 100 weight parts of the epoxy compound. Two weight parts of dibenzosuberone (sensitizer) was also added thereto. Then, the obtained mixture was stirred and mixed to prepare solution in which the epoxy compound, the sensitizer and the polymerization initiator were homogeneously dissolved in the solvent. The solution was fed to a brown colored cylindrical glass vessel having the inner diameter of 5mm ϕ and the length of 20mm to the depth of 10mm from bottom to prepare test sample. The test sample contained in the glass vessel was irradiated with U.V. light from upper liquid surface (8000mJ/cm²). The obtained hardened product was taken out by destroying the vessel, and the thickness of the hardened product was measured with a thickness gauge. The results were reported in the following Table 15.

The test sample contained in the vessel, which was prepared by using the same procedure as mentioned above, was irradiated with U.V. light (8000mJ/cm²). Then, the irradiated test sample was subjected to thermal treatment by maintaining the sample in a thermostat whose temperature was preset at 160°C for 1 hour. The obtained hardened product (5mm ϕ \times 10mm) was taken out from the vessel. The gel fraction of the hardened product was reported in the following Table 16.

Table 15

Ex. No.	Epoxy compound	Initiator	Thickness (mm)
112	phenol-novolak type	Ex. 3	0.98
113	ditto	Ex. 9	1.09
114	ditto	Ex. 11	1.73
115	ditto	Ex. 12	1.25
116	bisphenol F type	Ex. 3	1.25

117	ditto	Ex. 9	1.51
118	ditto	Ex.11	2.31
119	ditto	Ex.12	1.18
120	hydrogenated bisphnol A type	Ex. 3	1.35
121	ditto	Ex. 9	2.02
122	ditto	Ex.11	2.43
123	ditto	Ex.12	1.91

Table 16

Ex. No.	Epoxy compound	Initiator	Gel fraction(%)
124	phenol-novolak type	Ex. 3	96.2
125	ditto	Ex. 9	97.9
126	ditto	Ex.11	98.1
127	ditto	Ex.12	98.3
128	bisphenol F type	Ex. 3	95.4
129	ditto	Ex. 9	97.8
130	ditto	Ex.11	97.9
131	ditto	Ex.12	96.5
132	hydrogenated bisphnol A type	Ex. 3	96.9
133	ditto	Ex. 9	98.4
134	ditto	Ex.11	98.9
135	ditto	Ex.12	97.1

Industrial Applicability

The polymerization initiator of the present invention have such a unique property that it can initiate both photopolymerization and thermal polymerization when used in polymerizing cationically polymerizable organic substance, though the polymerization initiator comprises an identical crystalline ion-association substance.

In particular, since the photopolymerization initiator for organosiloxane has not almost been developed, the polymerization initiator of the present invention is valuable.

For the above-mentioned unique property of the polymerization initiator of the present invention, it is possible to obtain a merit in practical use; that is, after the U.V. light irradiation, it is possible

to carry out the hardening in shade zone which is not exposed to U.V. light or a deep zone to which U.V. light dose not reach by means of heating (photopolymerization plus thermal polymerization). This merit is very important, because, in accordance with conventional method, when the hardening is carried out by using both means of photopolymerization and thermal polymerization in accordance with conventional method, it is necessary to modify a monomer itself; for example, to prepare a modified organosiloxane having epoxy group.

Since the polymerization initiator of the present invention is effective equally to a plurality of cationically polymerizable organic substances (such as epoxy compounds, organosiloxane compounds, etc.), it can display its function to various mixtures consisting of a plurality of compounds having reactive groups of different type.

Therefore, it is possible to spread field and method for use of cationically polymerizable organic substances by using the polymerization initiator of the present invention.

03043-0310
T0E20-3E40330

What is claimed is:

1. (deletion)
2. (deletion)
3. (deletion)
4. (deletion)
5. (deletion)
6. (deletion)
7. A polymerization initiator for cationically polymerizable organic substance, characterizing that said polymerization initiator comprises a crystalline ion-association substance a general formula (I):

$$[\{C_5(R^1)_n\}_{2m}M_m]^{1+}[\{B(R^2)_4\}^-]_1$$
 wherein M is a transition metal of center nucleus; C₅ is cyclopentadienyl group; R¹ is electron donative or electron attractive substituent bonded to a carbon atom of cyclopentadienyl group, or an organic group bridging two neighboring carbon atoms; n is a number within range of 0 to 3; m is either 1 or 2; 1 is either 1 or 2; R² is a ligand coordinated to boron atom (B), and the four R²(s) are the same to each other.
8. The polymerization initiator claimed in the claim 7, wherein said cationically polymerizable organic substance is a compound or mixture of at least two compounds selected from among methylol compounds, ethylenic compounds, polyacetal compounds, organosiloxane compounds, polyamide compounds and heterocyclic compounds.
9. The polymerization initiator claimed in the claim 8, wherein said cationically polymerizable organic substance is selected from among organosiloxane compounds, epoxy compounds and mixtures thereof.
10. (deletion)
11. (addition) The polymerization initiator claimed in the claim 7, wherein said transition metal of center nucleus (M) of said general formula (I) is selected from a group consisting of Ti, Zr, Fe, Ru, Os, Hf, V, Cr, Mo and W.
12. (addition) The polymerization initiator claimed in the claim 7, wherein said electron donative or electron attractive substituent of said general formula (I) is, identical to or different from each other, selected from a group consisting of alkyl group, cycloalkyl group, alkoxy group, aryl group, dialkyl group, silyl group, acyl group, cycloalkenyl

053043 0711

group, aminogroup, carboxyl group, organoboranyl group, phosphino group, aldehyde group, hydroxyl group and vinyl group; and said organic group bridging two neighboring carbon atoms is alkylene group.

13. (addition) The polymerization initiator claimed in the claim 7, wherein the metallocene derivative cation having mono-nucleus structure or di-nucleus structure which constitutes the crystalline ion-association substance having the general formula (I) is selected from a group consisting of acetyl ferrocenium, tert.-amyl ferrocenium, benzoyl ferrocenium, n-butyl ferrocenium, cyclohexenyl ferrocenium, cyclopentenyl ferrocenium, 1,1'-diacetyl ferrocenium, 1,1'-di-n-butyl ferrocenium, N,N-dimethylaminomethyl ferrocenium, 1,1'-dimethyl ferrocenium, ethyl ferrocenium, (dihydroxyboranyl) ferrocenium, 1-hydroxyethyl ferrocenium, hydroxymethyl ferrocenium, vinyl ferrocenium, 1,1-bis(diphenylphosphino) ferrocenium, ferrocenium, t-butyl ferrocenium, dibutyl ferrocenium, bis(cyclopentadienyl) chromium cation, bis(cyclopentadienyl) molybdenum chloride cation, bis(cyclopentadienyl) osmium cation, bis(t-butylcyclopentadienyl) titanium chloride cation, bis(cyclopentadienyl) dicarbonyl titanium cation, bis(cyclopentadienyl) titanium chloride cation, bis(cyclopentadienyl) tungsten chloride cation, bis(i-propylcyclopentadienyl) tungsten chloride cation, vanadocenium, bis(n-butylcyclopentadienyl) zirconium chloride cation, bis(t-butylcyclopentadienyl) zirconium chloride cation, bis(cyclopentadienyl) zirconium chloride cation, bis(ethylcyclopentadienyl) zirconium chloride cation, bis(methylcyclopentadienyl) zirconium chloride cation, bis(indenyl) dimethyl zirconium cation, bis(t-butylcyclopentadienyl) hafnium chloride cation, bis(ethylcyclopentadienyl) hafnium chloride cation, bis(iso-propylcyclopentadienyl) hafnium chloride cation and diferrocenium derivative cation.

14. (addition) The polymerization initiator claimed in the claim 7, wherein said ligand (R^2) of the said formula (I) is selected from a group consisting of aryl group, halogenated aryl group, halogen haloform aryl group, cycloalkynyl group, halogenated cycloalkyl group, halogenated cycloalkynyl group, cycloalkyloxy group, cycloalkenyloxy

group, alkadienyl group, alkatrienyl group, alkynyl group, halogenated alkenyl group, halogenated alkadienyl group, halogenated alkatrienyl group, halogenated alkynyl group and heterocyclic group.

15. (addition) The polymerization initiator claimed in the claim 7, wherein said tetranentate borate complex anion which constitutes the crystalline ion-association substance having the general formula (I) is selected from a group consisting of tetrakis(4-fluorophenyl) borate anion, tetrakis(4-fluorobiphenyl) borate anion, tetrakis[3,5-bis(trifluoromethyl)phenyl] borate anion, tetrakis(3,5-difluorophenyl) borate anion, tetrakis[4-(trifluoromethyl)phenyl] borate anion, tetrakis(2,3,5,6-tetrafluorophenyl) borate anion, tetrakis(1,2,3,4,5-pentafluorophenyl) borate anion, tetrakis(3,4,5-trifluorophenyl) borate anion, tetrakis(3-fluoropropane) borate anion, tetrakis[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl] borate anion, tetrakis(2,4,6-trifluorophenyl) borate anion, tetrakis(nonafluorobutyl) borate anion, tetrakis(perfluorohexyl) borate anion, tetrakis(perfluoropentyl) borate anion, tetrakis(perfluorooctyl) borate anion, tetrakis(perfluoro-3-methylbutyl) borate anion, tetrakis(perfluoro-5-methylbutyl) borate anion, tetrakis(heptafluoropropyl) borate anion, tetrakis(3,5-dichlorophenyl) borate anion, tetrakis(4-chlorophenyl) borate anion, tetrakis(benzyl chloride) borate anion, tetrakis(chlorobenzyl) borate anion, tetrakis[2-(perfluorobutyl)ethyl] borate anion, tetrakis[2-(perfluorohexyl)ethyl] borate anion, tetrakis[2-(perfluorooctyl)ethyl] borate anion, tetrakis[2-(perfluoro-7-methyloctyl)ethyl] borate anion, tetrakis[2-(perfluoro-5-methylhexyl)ethyl] borate anion, tetrakis(2,2,3,3-tetrafluoropropyl) borate anion, tetrakis(1H,1H,5H-octafluoropentyl) borate anion, tetrakis(1H-perfluorohexyl) borate anion, tetrakis(1,1-difluoroethyl) borate anion, tetrakis[3,5-bis(trifluoromethyl)benzyl] borate anion,

0000435 03101

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled Novel Crystalline Ion-Association Substance, Process for Producing the Same, and Polymerization Initiator

the specification of which

(check one)

☐ is attached hereto.

☐ was filed on _____ as

Application Serial No. _____

and was amended on _____

(if applicable)

☒ was filed as PCT international application

No. PCT/JP00/00518 on January 31, 2000

and was amended under PCT Article 19 on July 19, 2000

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
<u>24294/99</u>	<u>Japan</u>	<u>01/02/1999</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
<u> </u>	<u> </u>	<u> </u>	<input type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
<u> </u>	<u> </u>	<u> </u>	<input type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

William H. Logsdon	22,132	Paul M. Reznick	33,059	Jesse A. Hirshman	40,016
Russell D. Orkin	25,363	John W. McIlvaine	34,219	James G. Porcelli	33,757
David C. Hanson	23,024	Michael I. Shamos	30,424	Kent E. Baldauf, Jr.	36,082
Frederick B. Ziesenheim	19,438	Blynn L. Shideler	35,034	Christian E. Schuster	43,908
Richard L. Byrne	28,498	Julie W. Meder	36,216	Deborah M. Altman	42,259
Kent E. Baldauf	25,826	Lester N. Fortney	38,141	Dean E. Geibel	42,570
Barbara E. Johnson	31,198	Randall A. Notzen	36,882	Thomas Clinton	40,561
				Nathan J. Prepelka	43,016

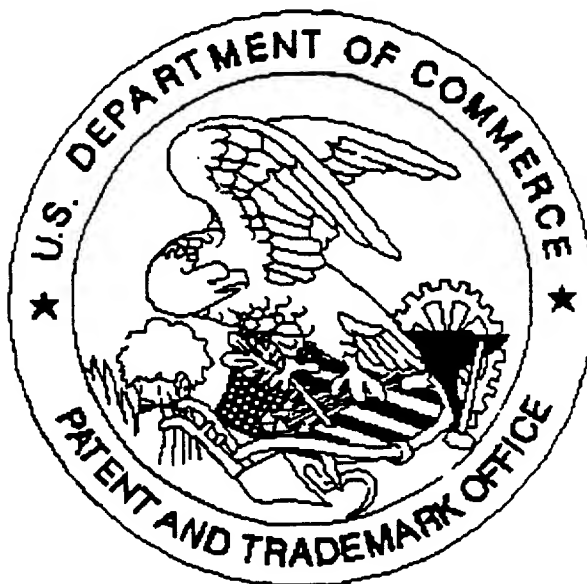
Send Correspondence to:

Russell D. Orkin, 700 Koppers Building, 436 Seventh Avenue, Pittsburgh PA 15219-1818

Direct Telephone calls to: (name and telephone number) Russell D. Orkin (412) 471-8815

Full name of sole or first inventor	Shin HIWASA
Inventor's signature	Shin Hiwasa
Date	July 11, 2001
Residence	c/o Autex, Inc., Technical Center, 4574-1, Shimoota, Shintonemachi, Inashiki-gun, Ibaraki 300-1424, Japan
Citizenship	JPX
Post Office Address	c/o Autex, Inc., Technical Center, 4574-1, Shimoota, Shintonemachi, Inashiki-gun, Ibaraki 300-1424, Japan
Full name of second joint inventor, if any	
Second inventor's signature	
Date	
Residence	
Citizenship	
Post Office Address	

United States Patent & Trademark Office
Office of Initial Patent Examination -- Scanning Division



Application deficiencies found during scanning:

☒ Page(s) 3 of Declaration were not present
for scanning. (Document title)

☐ Page(s) _____ of _____ were not present
for scanning. (Document title)

☐ *Scanned copy is best available.*

SCANNED, # 12